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SYSTEMS STUDY OF NITROGEN OXIDE CONTROL METHODS FOR STATIONARY SOURCES

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FOREWORD

This report summarizes the studies made by Esso Research and Engineering Company for the National Air Pollution Control Administration during the first phase of Contract No. PH 22-68-55. The work done under this contract covers the period between June 20, 1968 and January 5, 1969.

These studies were carried out in the Engineering Research Department of the Government Research Laboratory of Esso, under the management of Mr. Leonard Berkowitz. Dr. William Bartok was the contractor's project director.

The authors wish to acknowledge the help and comments received from the NAPCA project officers, Messrs. D. Bruce Herschel and Thomas C. Gilman, and the assistance provided by Dr. Chauncey C. Hale and Mrs. Gail D. Smith.

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1. SUMMARY

This interim report on a systems study of nitrogen oxide control methods for stationary sources is submitted to the Division of Process Control Engineering, National Air Pollution Control Administration, under Contract No. PH 22-68-55. The work done on this contract by Esso Research and Engineering Company covers the period between June 20, 1968, and January 5, 1969.

The systems study is being carried out in two phases. The first phase of the program has been aimed at the definition of the nature and magnitude of the stationary NO_x problem in the U.S. In the second, overlapping phase, existing and potential NO_x control techniques have been identified. This will be followed by the assessment of control technique possibilities, and the development of two alternate 5-year R&D plans for stationary NO_x control, in the amounts of $10 million and $50 million, respectively.

A comprehensive, selective review of the pertinent literature has been completed, resulting in over 600 items of specific interest. Information from the published literature has been complemented by field survey contacts, which led to additional information on NO_x emissions and control technique possibilities. A detailed questionnaire for steam-electric plants selected on the basis of geographic location and fuel type has been developed. The results of this questionnaire are expected to provide information on NO_x emission factors for fossil fuel burning power plants and background data for cost-effectiveness evaluations.

Nitrogen oxide emissions from combustion sources have been estimated by major sectors (including transportation) and fuel type, for the years 1950, 1955, 1960, 1965, 1970, 1975, 1980 and 2000. Stationary sources account for about 55% and transportation for 45% of uncontrolled emissions for the period 1950 through 1980. The contribution of power generation to the NO_x emissions from stationary sources is estimated to increase from 45% in 1965 to 57% in 1980 and 64% in the year 2000. These estimates are being refined to reflect effects of major technological changes, possible control methods, and the contribution of non-combustion sources.

Studies of NO_x control techniques have concentrated so far on the identification of promising methods. In addition to the limited amount of available technology for NO_x removal from stack gases, several new approaches have been identified with potential for simultaneous removal of sulfur and nitrogen oxides. In broad categories, decomposition, reduction, sorption and oxidation techniques have been studied. On strictly technical grounds, selective NO_x reduction techniques with ammonia or possibly with hydrogen sulfide, aqueous caustic scrubbing techniques, a modified version of the lead chamber acid process, and adsorption on some metal oxides appear to be promising. In spite of the attractive simplicity of catalytic NO_x decomposition, known catalysts lack sufficient activity for this reaction.

Combustion process modification techniques are felt to be potentially the simplest and least costly approaches to the NO_x control problem. However, demonstrated technology is quite limited at present. So far in the study, the existing control methods have been identified. In general, these techniques involve the modification of operating methods or design features. Low excess air combustion, flue gas recirculation, two-stage combustion, burner location and spacing, fluidized bed combustion are prime candidates for further study in this area. The applicability of specific techniques (alone or in combination with others) depends heavily on the type and size of combustion equipment, and on the type of fuel used. In this area the work to date has concentrated on collecting the information to be analyzed. Accordingly, the detailed evaluation of this highly important control technology sector has been deferred to the remainder of the contract period.

Formulation of a simple, idealized model for NO_x formation in combustion processes has been initiated. This study is aimed at the definition of requirements for more detailed combustion models, which could be used for guiding the design of combustion equipment emitting less NO_x.

2. INTRODUCTION

Nitrogen oxides in the atmosphere can participate in the formation of ozone and smog-forming reactions with hydrocarbons, under the influence of solar radiation. The air pollutant effects of nitrogen oxides (NO and NO_2) *per se* at concentration levels encountered in the atmosphere have not yet been clearly established. These effects are the subject of current investigations by a variety of research groups.

Both stationary and mobile sources emit oxides of nitrogen into the atmosphere. Based on prior estimates, roughly one-half of the total NO_x pollutants are emitted from stationary sources in the U.S. Of the stationary contributions, fossil fuel burning power plants may account for 40-50%.

To establish the character of the stationary NO_x control problem, Esso Research and Engineering Company has been granted a contract by the National Air Pollution Control Administration to conduct a systems study of nitrogen oxide control methods for stationary sources. This contract has the following objectives.

In the first phase of the program, the nature and magnitude of the stationary NO_x problem in the U.S. is being defined on a regional basis. Emission inventories are being compiled for all significant sources from 1950 to 1967, and projections to the year 2000 are being made taking into account technological, economic and socio-political trends.

Both existing and potential NO_x control technology will be assessed in the second phase of the systems study. Three broad categories of control techniques are covered: (1) combustion process modifications; (2) in-process removal of NO_x from flue or tail gases; and (3) other industrial process modifications. Also, the requirements for a mathematical model of NO_x formation in combustion processes will be defined to help guide the design of combustion equipment producing low NO_x emissions.

The final product of the systems study will be catalogues of control technology assessed on the basis of cost effectiveness. Two alternate 5-year research and development program plans will be developed for stationary NO_x emission control.

3. LITERATURE SURVEY

A review of the literature on NO_x and related topics through December 1968 has been completed to assemble a set of 2500 references and abstracts which are now being analyzed. A fairly liberal selection of references was made in this initial review, including basic information and background material to define the NO_x emission problem from stationary sources and establish possible control techniques. The information collected has been particularly useful to date in the statistical and control technology parts of the project.

The strategy for the literature review has been to start wherever possible with evaluated information, and get the best references as promptly as possible into the working files. The first step was to assemble a card file of some 400 references accumulated at the start of the project by the study team. These were derived from their previous expert knowledge and initial contacts with other experts in the company and in the field.

This file included a collection of references previously assembled by the NAPCA Project Officer, which provided working copies and additional references not already at hand. A comprehensive list of the 2194 U.S. patents issued since 1950 which mention NO_x was obtained from IFI-Plenum, in a computer based search programmed to highlight processes for NO_x removal and control. This provided a hundred references which were added to the file, and a complete title, number, and partial key-word analysis for all patents in the list.

The second step in the literature search started with a NAPCA card file of some 400 transcripts from Chemical Abstracts from 1956 through 1966, kindly transmitted to us by the Project Officer. This was particularly useful to fill out the file on NO_x reaction kinetics and mathematical modeling. Coverage was then extended in Chemical Abstracts through 1967 and 1968, by a complete paging of sections deemed most pertinent to the project. This started with the sections on air pollution, various oxides of nitrogen and nitric acid, and a parallel search of corresponding entries in the Engineering Arts Index. Coverage was next extended in the cumulative indexes of Chem. Abstracts from 1956 through 1966, to include these areas and pertinent entries on the chemistry of the oxides of nitrogen, and in the Engineering Arts Index starting in 1950.

The basis of selecting pertinent references was continually refined during this search by the team evaluation of material at hand. Copies of some 500 original references were provided to the team members for this purpose. A final check of Chemical Abstracts from 1956 back to 1907 and a third run-through for the period 1956 to date added pertinent references indexed under flames and combustion to the list of areas searched. This search is now complete for 1907 through 1968.

Special literature sources for pertinent material were also covered at the same time, such as the Penn State "Air Pollution Titles" starting in 1965 and the API "Subject Index to Current Literature on Air and Water Conservation" starting in 1967. Three visits to the Air Pollution Technical Information Center (APTIC) at Arlington provided references from their Termatrex index system on special topics. Numerous specialized indexes and proprietary information reviews were also consulted in our library, including previous Company reviews, Predicasts, SEARCH, and the Stanford Research Institute's Chemical Economics Handbook and Process Economics Reports which are not available for general circulation.

The searching strategy provided a continuous feedback of significant new references into the system, by the team members' selection of items from the bibliographies of the better references. The percentage of the "new" references from this or other sources which are found to be already in the file is now well over 80% in most areas. Special searching is being continued in a few areas, such as NO_x emissions from noncombustion sources, where this "familiarity index" for new references is still about 50%.

A preliminary bibliography of some 600 references is attached to this report, to summarize the evaluated output of the literature reviews as of January, 1969. This contains selected items listed alphabetically by author for each of five major areas of interest, with the title and reference for each item:

References 1-88:	NO_x Statistics and Forecasting
References 100-370:	NO_x Removal from Stack Gases
References 400-483:	Combustion Modifications
References 500-675:	Kinetics and Modeling
References 676-698:	General References

This bibliography is an informal transcript of headings taken from the abstract card files for selected items, "as is." It is subject to re-alphabetizing, editorial changes, and the addition of important references, which may be noted during the further study of the abstracts which appear on the cards. The present list has not been edited to a consistent style, and it includes informal references for a number of articles which are now in the files in the form of preliminary preprints or mimeographed reports. It is derived from a still-changing file, and its transient nature has been emphasized by the heading "Preliminary - January 1969" which appears on each page.

The abstract card file has been duplicated for convenience in three Xerox copies. The master file is kept in alphabetical order by author and used as the index for accession of original articles or Xerox copies, for distribution to individual team members. A duplicate author index is kept as a working file, and each team member has a working file of cards for his specific area. The fourth set is a working file for classification, which is currently being reworked for keywords-by-process. The primary object of this reworking is not to produce a finished file (except for the author index), but to pick up new concepts or viewpoints which should be considered in the further evaluation of the material at hand.

The total abstract file now includes the 600 items in the selected bibliography, a somewhat larger number which provide additional information on special topics, and others which will be rejected as irrelevant. There is also a large collection of general background references, not included in the present selection.

The present bibliography is, therefore, a first cut of the references expected to be most useful in drawing the conclusions and programs of our final report. The five separate headings of this bibliography are tentatively set as chapter headings to appear in the state-of-the-art review of that report.

4. CHARACTERIZATION OF THE NO_x EMISSION PROBLEM FOR STATIONARY SOURCES

The basic objective of Phase I is to define the nature and magnitude of the NO_x emission problem from stationary sources in the United States in sufficient depth to be useful in establishing required control technology R&D. Definition of the problem includes identification of NO_x emitters, determining their magnitude and distribution for the year 1950 through 1967, and making projections of their numbers and characteristics to the year 2000. Projections must consider technological trends, changing energy sources, population distribution and other socio-politic-economic factors. Major emphasis will be in the years 1967, 1980 and 2000. Detailed, accurate data for 1967 provide a solid basis for extrapolating current trends to the year 1980 as a convenient base point, since it is long enough to depend upon an estimate of future trends but not so long as to be very uncertain. The year 2000 is far enough in the future so that fundamental technological changes can take place, and it is necessary to consider morphological analysis and technological forecasting in addition to extrapolation of past and current trends. Thus, some current emitting sources such as household coal-burning furnaces will almost surely be eliminated in the year 2000, while new sources such as magnetohydrodynamic generation might well be an important power source for electricity generation.

Our initial evaluation of stationary emission sources has been guided by the four report volumes titled Emissions of Oxides of Nitrogen from Stationary Sources in Los Angeles County resulting from a joint District, Federal, State and Industry Project (676). This project indicated the following breakdown of sources:

Sources (in Los Angeles)	% of Total
Fossil Fuel Power Plants	44
Non-Power Boilers	22
Refinery Heaters	9
Stationary Internal Combustion Engines	7
Water and Space Heaters	6
Miscellaneous (Metallurgical and Other Furnaces, Chemical Plants, etc.)	12
Total	100

These data were obtained by establishing a census of emission sources and measuring actual emissions from a selected sample of each class of sources. The study showed that 44% of stationary emissions were due to power plants while another 22% came from non-power boilers. Thus, about two-thirds of NO_x emissions were due to power and non-power boilers. Although the national emission pattern was not expected to match the LA results exactly, subsequent studies have indicated the same general pattern. Thus, detailed plans were made to obtain data on boilers which would be useful for ranking boiler types and emission rates as well as providing a basis for evaluating control technology.

4.1. Survey of Steam-Electric Plants

Since power plants are the largest single source of NO_x emissions, detailed plans have been developed to obtain information on this industry. The centralized institutional and governmental agencies that have been surveyed by personal visits include the Edison Electric Institute, Electric World Magazine, Federal Power Commission, Americal Boiler Manufacturers Association, National Oil and Fuel Institute and the Bureau of Mines. Through these visits, literature studies, and discussions with experienced company engineers, we have developed the Steam-Electric Plant Survey Questionnaire-Attachment 1, Steam-Electric Plant Survey Instructions-Attachment 2 and Steam-Electric Plant Questionnaire, Example-Attachment 3. The questionnaire has been divided into Section I-Boiler Information, Section II-Two Stage Combustion Information Sheet and Section III-Peak Shaving Units (Gas Turbines-Internal Combustion Engines). The final details of the questionnaire were established through detailed discussions with representatives of the electric utility industry.

Nineteen of the largest utilities in the nation have been selected to receive this questionnaire. Factors used in evaluating which companies were to be included in the sample were: size (net power generated), type of fuel used, geographic location, and availability of emission inventory data by Air Quality Control Region. Federal Power Commission data has been recorded for boilers on steam pressure, maximum steam rating, initial year of operation, manufacturer and type of firing. Data available on peak shaving units (gas turbines and internal combustion engines) include unit number, nameplate rating, year installed, manufacturer, fuel consumption at full load, exhaust gas temperature and inlet gas temperature. All of the other data on the questionnaire will be obtained by contacting the individual companies. Visits will be scheduled as soon as final approval from NAPCA is obtained.

4.2. Other Emission Survey Plans

Since our survey plans covering electric power emissions have been largely completed, we are now in a position to concentrate on the major industrial, household, and commercial sectors. Responsibility for the following sectors have been assigned to individual team members: Electric Power Industry, Petroleum Refining, Pulp and Paper Industry, Chemical Industry, Cement Manufacture, Glass (including stone and clay), Food, Stationary Internal Combustion Engines, Incineration, Domestic & Commercial Heating and Other Sources.

An effort will be made to obtain data on emission factors, fuel use (power, heat and process) and important control variables affecting emissions in each of these sectors. In addition, data on number, size and location of companies and their plants will be sought so that representative surveys can be planned where needed because of lack of definitive data. These data also will be useful in increasing the efficiency of field surveys where it is possible to survey several sources at a single location, (cluster sampling) resulting in less trips for the same size sample.

4.3. Preliminary Estimates of NO_x Emissions in the United States

Preliminary estimates of the magnitude and character of the NO_x control problem from combustion sources have been determined for the years 1950, 1955, 1960, 1965, 1970, 1975, 1980 and 2000. Attachments 4 through 10 provide these data on total United States (50 states) NO_x emissions by major sectors (household and commercial, industrial, electric generation and transportation) and fuel source (natural gas; liquidified gases; kerosene, distillate and residual fuel oils; coal and lignite; refuse burning; gasoline; and jet fuel). These tables have been calculated from published data on fuel consumption and emission factors with our own estimates added where necessary, as shown in the footnotes to each table.

The emission factors used in our calculation are shown below in Table 1 and are derived from Public Health Service Publication No. 999-AP-42 Compilation of Air Pollution Emission Factors by R. L. Duprey, 1968. (Table 3 lists emission factors on a uniform basis for ready comparison purposes, i.e. pounds NO_x per 10^9 BTU of fuel heating values.) The fuel quantities are taken from the Bureau of Mines Information Circular 8384 An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projection and Forecasts to the Years 1980 and 2000 by Warren E. Morrison and C. L. Readling, July 1968. These forecasts have been compared with a number of published and private sources. The Bureau of Mines figures are close to the median of all forecasts available.

TABLE 1

NO_x EMISSION FACTORS

	Household and Commercial	Industry	Electric Generation	Transportation
1. Natural gas[1p6]	116 lb/10^6 ft^3 (58 tons/10^9 ft^3)	214 lb/10^6 ft^3 (107 tons/10^9 ft^3)	390 lb/10^6 ft^3 (195 tons/10^9 ft^3)	--
2. Coal[1p5]	8 lb/ton (4 tons/1000 tons)	20 lb/ton (10 tons/1000 tons)	20 lb/ton (10 tons/100 tons)	
3. Jet Fuel[1]	--	--	--	23 lb/Flight Conv. 9.2 lb/Flight Fan-jet
4. Gasoline[1]	--	--	--	113 lbs/1000 gals (2373 tons/10^6 BBL)
5. Kerosene[2]	12 lb/1000 gal (252 tons/10^6 BBL)	72 lb/1000 gal (1512 tons/10^6 BBL)	--	
6. Distillate[2]	12 lb/1000 gal (252 tons/10^6 BBL)	72 lb/1000 gal (1512 tons/10^6 BBL)	--	222 lb/1000 gal 4662 tons/10^6 BBL)
7. Residual[1p7] Fuel Oil	12 lb/1000 gal (252 tons/10^6 BBL)	72 lb/1000 gal (1512 tons/10^6 BBL)	104 lb/1000 gal (2184 tons/10^6 BBL)	222 lb/1000 gal (4662 tons/10^6 BBL)
9. Refuse[1p10]	2 lb/ton	2 lb/ton	--	--

(1) R. L. Duprey, Compilation of Air Pollutant Emission Factors, PHS No. 999-AP-42, 1968.

(2) Fuel Oil Emission Factors Used.

To illustrate how the tons of NO_x emissions were calculated, consider NO_x emissions from natural gas combustion in the Household and Commercial Sector for the year 1950 shown in Attachment 4 as 91,000 tons. The emission factor for natural gas consumption for domestic and commercial heating units is 116 lbs NO_x per million cubic feet of natural gas burned or 58 tons per billion cubic feet.* With 1,568 billion cubic feet of natural gas consumed in this sector, the estimated tons of NO_x emitted is equal to 1,568 x 58 = 90,944 or 91,000 tons rounded off to the nearest 1,000 tons. Similar type calculations were made for kerosene, distillate and residual fuels; coal and lignite, and gasoline for the various consuming sectors. In the case of liquified gases, the emissions were calculated on a B.T.U. basis as shown in footnote 3. Refuse burning was calculated on the basis of four pounds of refuse per capita day. NO_x emissions from jet fuels were based on an emission of 20 pounds NO_x per flight with the number of flights estimated using published data on revenue passenger-miles.*

* "Resources in America's Future", by H. H. Landsberg et al., Johns Hopkins Press, 1963.

Table 2, below, summarizes NO_x emissions in thousands of tons from Attachments 4 through 10 for the major sectors: Household and Commercial, Industrial, Electric Generation, Total Stationary Sources, Transportation, and Grand Total.

TABLE 2

NO_x EMISSIONS FROM COMBUSTION ASSUMING NO CONTROL

(Thousands of Tons Expressed as NO_2)

Year	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total
1950	724	1,877	1,274	3,875	3,557	7,432
1955	657	2,086	1,842	4,585	4,643	9,228
1960	664	2,856	2,303	5,823	4,871	10,694
1965	707	3,267	3,162	7,137	5,509	12,646
1970	765	3,380	3,966	8,111	6,529	14,640
1975	849	3,526	5,045	9,420	7,768	17,188
1980	966	3,768	6,409	11,143	9,193	20,336
2000	1,450	3,579	8,879	13,908	18,488	32,396

Table 2 indicates that NO_x emissions from major combustion sources amounted to about 7.5 million tons in 1950, 9 million tons in 1955, 11 million tons in 1960 and 13 million tons in 1965. The projected figures based on extrapolation of current economic and technological trends are 15 million tons in 1970, 17 million in 1975, 20 million in 1980 and 32 million tons in the year 2000. Stationary sources account for about 55% of the emissions and transportation about 45% for the period 1950 through 1980. The electric generation sector accounts for an estimated 33% of the stationary sources in 1950. However, because of its rapid growth, electric generation continuously increases as a proportion of the stationary sources to 39% in 1960, 45% in 1965, 48% in 1970, 53% in 1975, 57% in 1980 and 64% in the year 2000. It has been assumed in these calculations that hydropower plus nuclear power account for 17% of the gross energy input to electricity generating utilities in 1965, 29% in 1980 and 67% in the year 2000.

Tables similar to Attachment 4 through 10 have been calculated for each of the 50 United States for the years 1960 and 1965. These emissions will be analyzed in some detail by multiple regression models in order to establish a firm basis for projection purposes. Preliminary studies show that for the year 1960, 90% of the variation in total NO_x emissions for combustion for the 50 States is explained by or related to total State population. It was also found that car registrations explain about 90% of the variations in NO_x emissions for transportation. Adding variables such as heating degree-days and measures of industrial activity should result in improved correlations.

4.4. Morphological Analysis of Technological Forecasts

An initial, morphological analysis has been made of possible technological forecasts for the years 1980 and 2000. This type of analysis is useful in indicating the extreme range of NO_x emissions that might result from alternative energy uses in the relatively distant future.

To perform this analysis, all combinations of 6 Electric Generation alternatives, 3 Transportation alternatives and 4 Industrial, Household and Commercial alternatives have been calculated. The Electric Generation alternatives are:

U-1. Conventional steam boilers fired with oil, gas and coal, hydro-power generation and nuclear generation.

U-2. Conventional steam boilers fired with natural gas only, at 9,288 BTU/KWH in 1980 and 8,388 BTU/KWH in 2000.

U-3. Conventional steam boilers fired with bituminous coal only, at 8600 BTU/KWH in 1980 and 7700 BTU/KWH in 2000.

U-4. Conventional steam boilers fired with residual fuel oil only, at 9,495 BTU/KWH in 1980 and 8,595 BTU/KWH in 2000.

U-5. Conventional steam boilers fired only with present-type water cooled nuclear reactors.

U-6. Electricity generated from hydrocarbon-air fuel cells using natural gas as source fuel.

The three Transportation alternatives are:

T-1. Conventional automobiles and trucks.

T-2. Electric battery vehicles using utility electricity with an average efficiency of 42%.

T-3. Hydrocarbon-air fuel cell powered vehicles.

The four Industrial, Household and Commercial alternatives are:

I-1. Conventional combustion processes using all fossil fuels.

I-2. Conventional combustion processes but only using natural gas as fuel.

I-3. Fuel cells fired with natural gas.

I-4. All electric, utility generated.

The results of this analysis are shown in Attachment 11 for the year 1980 and Attachment 12 for the year 2000. The data in the body of the tables are estimated United States NO_x emissions in millions of tons from stationary sources, transportation sources and total stationary plus transportation sources. These results were calculated using current emission factors, and assuming no NO_x emission controls.

Examining Attachment 11, we see that for case I-1/T-1/U-1 (all sectors using conventional combustion technology), the estimated uncontrolled NO_x emissions would be 11.1 million tons from stationary sources and 9.2 million tons from transportation sources for a total of 20.3 million tons. However, if we assume that transportation (T-2) consists of electric vehicles powered by batteries charged from conventional utility (U-1) electricity, total NO_x emissions would increase to 23.4 million tons. In this case, (I-1/T-2/U-1), increased NO_x emissions from utilities would more than offset the decrease to zero of transportation NO_x emissions. Proceding to case I-1/T-3/U-1 where transportation is assumed to be powered by non-NO_x emitting fuel cells, the total emissions are estimated to be 11.1 million tons or at about the 1960 emission level. Case I-1/T-1/U-2 produces higher emissions than the base case, (I-1/T-1/U-1), since it is assumed that there is no hydro- or nuclear-generated electricity in U-2. The effect of fueling utilities with a single fuel, coal (U-3) or fuel oil (U-4), compared with natural gas (U-2), results in total NO_x emissions of 52.3 million tons for coal, 50.6 for fuel oil vs. 37.8 using natural gas. Future work will seek to determine which of these alternatives is the most likely.

4.5. Accuracy of Emission Estimates

The emission estimates in exhibits 1-12 should be considered as preliminary estimates which may be extensively revised before our final report is published. There are a number of possible additions and improvements which we plan to investigate: estimates of non-combustion sources such as nitric acid plants and fertilizer plants will be added; current emission factors will be revised, if possible, taking into account our steam-electric survey results on tested emissions for various types and sizes of boilers, as well as projected use of currently available control technology; forecasted fuel volumes will be further analyzed and compared to recently published and privately obtained forecasts; local emission survey results will be analyzed and results incorporated into our forecasting models, etc.

To illustrate the magnitude of the adjustments that may result, consider the accuracy of the published emission factors that were used in developing our emission estimates. Emission factors, for the most part, have been used to represent average emission rates for a particular type of fuel for a particular consumption sector. No adjustments have been made in our preliminary emission estimates for possible changes in average emission factors due to average changes in type and size of equipment, operating rates, control equipment, etc., over time.

Recently obtained private data indicate that these factors may be highly significant. In Table 3 the pounds of NO_x emitted per billion BTU for 3 fossil fuels burned in the three sectors - Household and Commercial, Industry and Electric Utilities according to published PHS emission factors can be used to illustrate the problems encountered in applying these factors to emissions from individual units.

TABLE 3

NO_x EMISSION FACTORS

(Pounds $NO_x/10^9$ BTU)

Fuel	Household and Commercial	Industry	Electric Generation
Natural Gas (1,046 BTU/Cu Ft)*	111	205	373
Coal (11,867 BTU/pound)*	337	842	842
Fuel Oils (149,966 BTU/gal)*	80-480	480	680

Thus (assuming equal efficiencies), these emission factors indicate that coal produces between 0.7 and 4.2 times as much NO_x emissions as fuel oil in household and commercial combustion, 1.8 times as much NO_x emission as fuel oil in industrial combustion and 1.2 times as much NO_x as fuel oil in electric generation combustion. Adjusting for average efficiencies would make only a small change in these ratios. For example the average number of BTU/KWH generated for gas, coal and oil in 1966* was 10,774, 10,301, and 11,247 respectively. Therefore, the pounds of NO_x emitted per 10^5 KWH from gas, coal and oil would be 402, 867 and 765 pounds respectively. Thus on a KWH basis, coal produces 1.13 times as much NO_x as oil compared to 1.24 times on a BTU basis; on a KWH basis coal produces 2.15 times as much NO_x as natural gas compared to 2.25 times on a BTU basis.

However, recently acquired data indicate how widely individual units may depart from the average emission factors. Listed below are the average NO_x emissions (ppm corrected to 3% excess O_2) at full load for six boiler units from a large public utility.

TABLE 4

PPM NO_x (ASTM 1608-60)

Unit	A	B	C	D	E	F	Ave.
Gas Fuel	760	300	620	410	450	135	449
Cracked Resid. Fuel Oil	430	300	440	340	580	190	380
Low Sulfur Fuel Oil	215	185	250	--	380	--	--
Res. F.O. To Gas Ratio	0.57	1.00	0.71	0.83	1.29	1.41	0.85

* Total United States BTU content from:
Steam-Electric Plant Factors/1968 Edition
National Coal Association, Washington,
D.C., October 1968. p. 46.

Four of the six units emitted less NO_x when burning residual fuel oil than when burning gas. Residual fuel oil to gas NO_x ratios varied from 0.57 to 1.41 with an average of 0.85 compared to a ratio of 2.25 from Table 3 calculated from published emission factors on a BTU basis. This example emphasizes the necessity (and difficulty) of obtaining realistic emission factors. We are hopeful that the use of our steam-electric questionnaire will enable us to narrow down this extreme variation. However, it appears more and more likely that additional emission data based on a well designed statistical sample of boiler units will be necessary for accurate emission surveys and to properly guide the research and development program on control methods.

4.6. Emission Source Surveys

The NAPCA office in Durham, North Carolina has sent us draft reports of recent emissions' source surveys for the following areas:

1. Cincinnati-Hamilton-Middleton, Ohio
2. Minneapolis-St. Paul, Minnesota
3. North Central Ohio
4. St. Louis, Missouri
5. Washington D.C. Metropolitan Area
6. New York-New Jersey Air Pollution Abatement Activity
7. Ironton, Ohio--Ashland, Kentucky--Huntington, West Virginia
8. Boston, Mass.
9. Dayton, Ohio
10. Denver, Colorado
11. Philadelphia, Pennsylvania
12. Pittsburg Metropolitan Area
13. Buffalo, New York
14. Seattle-Tacoma, Washington
15. Louisville Metropolitan Area
16. Metropolitan Indianapolis
17. Providence-Pawtucket-New Bedford-Fall River
18. Milwaukee

In addition we have obtained surveys from the following additional areas during our field trips and literature surveys:

19. Delaware Valley
20. Allegheny County, Pennsylvania
21. Bay Area Air Pollution District, California
22. County of Los Angeles Air Pollution Control District
23. Akron and Barberton, Ohio
24. Erie County, New York
25. Southwestern Ohio - Northern Kentucky
26. Niagara County, New York
27. Westchester County, New York

These reports will be very useful in our Phase I survey efforts both for geographic breakdowns and to aid in our correlation analyses.

5. NO$_x$ EMISSION CONTROL BY REMOVAL FROM STACK GAS

A broad category of potential nitrogen oxides emission control techniques involves the in-process removal of these oxides from stack gases. Nitrogen oxides are present in these gases in low concentration, as shown in Table 5.

Table 5

Typical Compositions of Stack Gases

	Volume %			
	Combustion of			Nitric Acid Manufacture, Pressure Process(d)
Component	Coal(a)	Oil(b)	Gas(c)	
N_2	76.2	77.0	72.3	96.0
CO_2	14.2	12.0	9.1	--
H_2O	6.0	8.0	16.8	0.7
O_2	3.3	3.0	1.8	3.0
SO_2	0.2	.15	--	--
NO_x	⟵ .07(e) ⟶			.3
% NO_x as NO (remainder as NO_2)	⟵ 90-95 ⟶			25-65
Particulates grams/ft^3	0.5(f)	0.01	--	--

a. Calculated for burning with 20% excess air a typical high volatile bituminous coal of the following composition: carbon-70.1%, oxygen-6.6, hydrogen-4.9, nitrogen-1.4, sulfur-3.0, ash-12.7, H_2O-1.3.

b. Calculated for burning a typical residual fuel oil of the following composition: 86.5% carbon, 10.3% H, 2.5% S, 0.7% N with 20% excess air.

c. Calculated for burning natural gas with 10% excess air.

d. Reference 692.

e. This is an average value. Actual values range from .02 to .15%.

f. Assumes 90% particulates removal.

Although seven different oxides of nitrogen are known, gas analyses indicate that only two--nitric oxide (NO) and nitrogen dioxide (NO_2)--are present in any significant amounts in these gases. In the gas from combustion processes, ninety percent or more of the nitrogen oxides are present as nitric oxide (466, 467, 483) which is colorless. Upon release to the atmosphere, nitric oxide is slowly oxidized to brown nitrogen dioxide. In nitric acid manufacturing plants or plants using nitric acid, from 35 to 75 percent of the emissions are NO_2 (692), with 50% being an overall average.

Even though the concentrations of nitrogen oxides are low in flue and tail gases, the volumes of gas emitted by some sources are so large that they individually release significant amounts of these contaminants.

Table 6

Quantities of Gas and NO_x Emitted by Different Sources

Source	Volume of Gas Released, 10^6 SCFH	NO_x Released (as NO_2) Tons/Hr
700 T/D Nitric Acid Plant	3.6	0.70
200 MW Coal Fuel Power Plant	22	1.0
1000 MW Coal Fuel Power Plant	110	5.0

Processing such large volumes of gas for NO_x control, particularly those from power plants, presents formidable engineering problems in gas contacting, equipment size, pressure drop, temperature control, etc. In addition to these general problems, the control of nitrogen oxides presents many specific and difficult problems because of their low concentration, their chemical and physical properties, and the interfering action of other species present in stack gases. Moisture, carbon dioxide, sulfur dioxide, and oxygen are present in greater concentrations than the nitrogen oxides. These prevent the use of certain sorption, scrubbing or catalytic processes or at least make their use much more difficult. Particulates present similar problems. These factors combine to make the removal of nitrogen oxides from stack gases very difficult. In spite of this, our study to date has identified a number of existing and potential stack gas emission control techniques.

Sections 5.1 to 5.5 of this report discuss these techniques in detail. Some general processes and cost considerations are reviewed. Detailed process designs and cost estimates will be made in the second part of this study.

5.1. CATALYTIC DECOMPOSITION

Because of its potential simplicity, the catalytic decompositon of nitrogen oxides to nitrogen and oxygen has obvious advantages as a control technique. Thermodynamically, this decomposition is favored at all but very high temperatures. Table 7 shows the calculated concentrations of nitrogen oxides in equilibrium with air and flue gas at different temperatures.

Table 7

Calculated Equilibrium Concentration of Nitrogen Oxides, ppm(a)

	Air		Flue Gas(b)	
Temp., °F	NO	NO_2	NO	NO_2
80	3.4×10^{-10}	2.1×10^{-4}	1.1×10^{-10}	3.3×10^{-5}
980	2.3	.71	.77	.11
2060	800	5.6	250	.87
2912	6100	12	2000	1.8

(a) Based on values in Ref. 220

(b) 3.3% O_2, 76% N_2 in flue gas

The fact that nitrogen oxides do not revert back to their elements as stack gases cool is due to the fact that decomposition is very slow, even when catalyzed. In a very long-lived experiment on NO decomposition, Howard and Daniels (214) in 1917 sealed NO in tubes with a wide assortment of catalysts. Fifty years later, no detectable decomposition was found at room temperature.

A number of investigators have studied the kinetics and mechanism of NO_x decomposition and have obtained different results. Green and Hinshelwood (203) investigated the decomposition on a heated platinum wire. Over the temperature range of 1000 to 1500°C, they determined the reaction to be unimolecular, unaffected by nitrogen but retarded by oxygen. Bachman and Taylor (126), who carried out the decomposition over platinum-rhodium, also found the decomposition to be retarded by oxygen, but bimolecular with respect to nitric oxide. Vetter (355) studied the decomposition of nitrogen oxides in a flow system between 927 and 1627°C and found a catalytic effect of oxygen on the reaction. Wise and Frech (672, 673) in their studies concluded that the thermal decompositon of nitric oxide was predominantly heterogeneous and unimolecular below 1000°K and homogeneous and bimolecular above 1400°K. They observed a similar catalytic effect of oxygen as had Vetter and explained it on the basis of a chain reaction mechanism involving oxygen atoms reacting in the initial step with NO. Kaufman and Kelso (230) and later Yuan, et al., (363) disputed this contention of oxygen enhancing the reaction. Yuan and coworkers also observed the reaction to be heterogeneous and zero order below 1100°C and homogeneous and bimolecular above 1800°C. Fraser and Daniels (141) measured the decomposition of 10% NO in helium at temperatures ranging from 740 to 1040°C on Al_2O_3, CaO, Cr_2O_3, Ga_2O_3, ZrO_2, Fe_2O_3, TiO_2, and ZnO catalysts. They found the decomposition to be zero order in this temperature range and obtained the rates shown in Table 8.

Table 8

Rates of Decomposition of NO per Gram of Cat. at 1040°C

Catalyst	Zero Order Rate of Decomposition (g moles/liter/sec/gr.cat)
Ga_2O_3	198×10^{-6}
Al_2O_3	94.8×10^{-6}
CaO	32.3×10^{-6}
ZrO_2	5.5×10^{-6}
Cr_2O_3	5.4×10^{-6}
Fe_2O_3	$.9 \times 10^{-6}$
ZnO	$.7 \times 10^{-6}$

Comparatively little published work is available on decomposition of nitric oxide when present in low concentrations as is the case for stack gases. Sakaida, et al (307), studied the decomposition of NO at a concentration of about 4000 ppm in nitrogen, on alumina pellets impregnated with either .1% platinum oxide or 3% nickel oxide. In the range of 800 to 1000°F and a pressure range of 1 to 15 atmospheres, the reaction was found to be second order with respect to nitric oxide, retarded by atomic oxygen and further retarded by excess nitrogen. Sourirajan and Blumenthal (328) investigated the decomposition reaction with 300 to 2100 ppm nitric oxide diluted with nitrogen over cobalt and copper oxide supported catalysts at temperatures in the range of 300 to 1000°C. Copper oxide deposited on silica gel was found to be the best catalyst. With this catalyst, 69% NO decomposition was obtained at 950°F and a low space velocity of 1320 V/V/hr from a gas containing 892 ppm NO in N_2. Other supports investigated were kieselguhr and alumina.

The most extensive screening study of NO decomposition catalysts for which results have been published is that by Riesz, et al. (298) at the Illinois Institute of Technology's Research Institute (IITRI). In this study, 21 commercial catalysts and 17 laboratory-prepared alumina supported catalysts were evaluated using a gas mixture containing 2000 ppm NO in N_2. The results of this work, summarized in Tables 9, and 10, indicated little or no reaction in all cases at the high space velocities used (i.e., about 120,000 V/V/Hr.).

Table 9

Results of IITRI's Study of Nitric Oxide Decomposition Catalysts - Commercial Catalysts

Catalyst	Catalyst Manufacturer	Decomposition Temp., °F					
		932		1112		1292	
		SV(a)	% NO Decomp	SV	% NO Decomp	SV	% NO Decomp
Magnesia-alumina spinel (27-70%)	Norton, LMA-520	1880	3	2075	4		
Silica-alumina (88-12%)	Universal Oil Products	1490	4				
Silica-phosphoric acid (70-30%)	Universal Oil Products, No. 2	1940	0	2025	0		
Vanadia-silica potassium sulfate (10-65-23%)	Davison Chemical, 903	1825	0	1785	0	1785	0
Vanadia-alumina (7-93%)	Harshaw Chemical, V-X-L533	38	20				
Hopcalite	Mine Safety Appliances	1450 135	0 0				
Chromia-alumina (19-81%)	Harshaw Chemical, CR-0205	1955	0	2140	0	2100	0
Ferric oxide	Girdler G3, carbon monoxide shift	1930*	2				
Magnetite	Tennessee Valley Authority, Ammonia synthesis	2000	0				
Nickel oxide ($NiO-SiO_2$)	Universal Oil Products, hydrogenation	1820	7	1935	3		
Cobalt-molybdate ($Co-MoO_3-Al_2O_3$)	Harshaw Chemical, Co-Mo-0401 desulfurization	1840 930	0 0				
Copper Oxide-alumina (10-90%)	Harshaw Chemical, Cu-0801	1255	3	1670	0		
Zinc oxide (99%)	Harshaw Chemical, Zn-0401	1870	0	1870	5		
Mossy zinc	Baker	2140	4				
Molybdena-alumina (10-90%)	Harshaw Chemical, Mo-1202	1795	7	2045	2		
Palladium-alumina (0.5-99.5%)	Baker	1900	1	1550	3	1910	1
Silver oxide-alumina (20-80%)	Harshaw Chemical, Ag-0301	1635	0	1620	0	1430	0
Tungstic oxide-alumina (10-90%)	Harshaw Chemical, W-0101	1680	0				
Platinum-asbestos (5-95%)	Baker	2000	18	2000	10	2140	7
Platinum-alumina (0.5-99.5%)	Baker	1770	5	2080	0	2085	0
Platinum-alumina (0.6-99.4%)	Baker, dehydrogenation	2140	0	1770	0	1890	0

---

* 250°C.

(a) Volumes of gas per minute per volume of catalyst.

Table 10

Results of IITRI's Study of Nitric Oxide Decomposition Catalysts - Laboratory-Prepared Catalysts

			Decomposition Temp, °C					
			932		1112		1292	
	Composition							
Catalyst	Oxide	Alumina*	SV	% NO Decomp	SV	% NO Decomp	SV	% NO Decomp
Sodium oxide-alumina	10	90	1835	1	1970	0	1835	1
Potassium oxide-alumina	5	95	1840	3	1815	0	1820	0
Potassium oxide-alumina	15	85	2250	2	2090	1	2045	1
Chromium oxide-alumina	10	90	1835	0	1870	0	2060	0
Manganese oxide-alumina	10	90	2045	0	1685	0	2130	0
Iron oxide-alumina	10	90	1690	0	2000	0	2090	0
Cobalt oxide-alumina	10	90	1860	0	1860	0	1955	0
Nickel oxide-alumina	10	90	1575	2	1685	2	1815	3
Copper oxide-alumina	10	90	1605	0	1635	0	1550	5
Zinc oxide-alumina	10	90**	1955	1	2090	1	2140	1
Strontium oxide-alumina	10	90	1910	0	1585	0	1585	0
Silver oxide-alumina	10	90	1665	0	1815	0		
Cadmium oxide-alumina	10	90	1740	0	2205	0	2220	0
Barium oxide-alumina	2.5	97.5	2140	0	1845	0	1955	0
Lead oxide-alumina	5	95	1940	0	1845	4	1860	5

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* Harshaw Chemical, Al-0401

** Alcoa, XH-151

Catalyst screening with an actual flue gas was carried out by Haagen-Smit at Southern California Edison's El Segundo Power Station. In searching for flue gas desulfurization and NO_x decomposition catalysts, Haagen-Smith evaluated over twenty different materials (shown in Table 11) using actual power plant flue gas from which only particulates have been removed. Of the materials tested, only copper oxide showed promise as a decomposition catalyst, providing a little more than 10% decomposition at test conditions (368).

Table 11

Catalysts Evaluated at Southern California Edison Co. (368)

	Temp., °F	Space Vel. ft^3/gr cat/hr
Harshaw Activated Alumina - AL 0104T	150-1400	.06
Harshaw Chrome-Alumina - CR 0205	350-1500	.06
Cr $(NO_3)_3$ on Harshaw - AL 104T	200-1600	.05
Chromic Oxide on Berl Saddles	350-1400	.02
Copper Wire	600-1350	.09
Copper Oxide (CuO)	450-1350	.04
Copper Chromite on		
- Berl Saddles	Unavailable	
- $MgO-Al_2O_3$ Spinel	Unavailable	
Ferric Chloride on Ceramic Support	Unavailable	
Steel Wool	600-1400	.02
Linde Mol. Sieves		
4A	150/700	.06-.15
5A		
13X		
Sodium 2-Phosphate-18-Molybdate on Alundum	500-1200	.08
Harshaw Molybdenum Alumina MO 1207	300-1300	.06
UOP NiO_2-SiO_2 Hydrogenation Cat.	200-1000	.04
Houdry Platinum	400-500	.05
KNO_3 on Alundum	350-1250	.09
$NaNO_3$ on $MgO-Al_2O_3$ Spinel	200-1200	
Harshaw Vanadium VO501S	500-1350	.06
Monsanto Vanadium	700-1100	.12

Copper oxide was also evaluated as a nitric oxide decomposition catalyst by Wikstrom and Nobe (361). Using cupric oxide supported on alumina, they reported being able to decompose as much as 50% of 1260 ppm NO_2 to nitrogen and oxygen at a space velocity equivalent to about 350 SCFH/lb catalyst and a temperature of 970°F. Since this study was carried out with air as the diluent, it is particularly interesting since any inhibiting effects of oxygen on reactivity should be reflected in the results. Attempts by researchers at Esso Research to reproduce these experimental data, however, have met with no success.*

Under a NAPCA grant, Walling (369) is studying the decomposition of nitric oxide by a number of commercially produced catalysts at 300, 600, and 800°F and at a space velocity of about 3400 V/V/hr. He has used a SO_2-free simulated flue gas containing 500 ppm NO, 3% O_2. The catalysts he has tested to date are shown in Table 12.

Table 12

Decomposition Catalysts Evaluated by Walling

Harshaw V_2O_5 catalyst (V-0301)
Harshaw CuO catalyst (Cu 0803)
Harshaw Mo_2O_3 catalyst (Mo 1202)
Girdler Ba-promoted $CuCr_2O_4$
Girdler $CuCr_2O_4$
Girdler Cr-promoted Fe_2O_3
Girdler NiO catalyst (H-219)
Fisher reagent Co_3O_4
Fisher reagent Fe_2O_3
Fisher reagent MnO_2
Fisher reagent CeO_2
Baker 5% platinum on asbestos

Walling's results indicate that these materials have little effect on the NO level of the gas at 300 and 800°F. At 600°F, the NiO, Co_3O_4 and platinum asbestos show initial NO removal, but this removal falls off to zero with continued use. This indicates that the initial removal observed is probably due to a surface sorption or reaction rather than true NO decomposition.

It is obvious from the foregoing discussion that there has been considerable research on NO decomposition, but only very limited success in finding a good catalyst for the reaction. This is the more discouraging, in light of the fact that most of the work to date has been carried out in the absence of SO_2 - a known poison for many catalysts. SO_2 would be present, even in "desulfurized" flue gas resulting from the combustion of coal or oil. Nevertheless, the possibility of finding a suitable catalyst cannot at this point be completely ruled out, and the incentive of a potentially simple, low cost decomposition process makes additional research in this area worthwhile.

*Private Communication

5.2. CATALYTIC REDUCTION

The reduction of nitrogen oxides can be classified as either selective or non-selective. In the former, NO is preferentially reduced in the presence of oxygen. In the latter case, the oxygen must first be consumed before the NO reduction will take place. Selective reduction is preferred as a control technique, since most NO_x containing gases contain more oxygen than nitric oxides (Table 5).

5.2.1 Non-Selective Catalytic Reduction

Non-selective catalytic reduction is being used in a number of nitric acid manufacturing plants for nitrogen oxides emission control. Two types of reduction are practiced - decolorization and abatement. Decolorization involves reducing NO_2 to colorless NO and is accompanied by the reduction of some oxygen. In non-selective abatement, all nitric oxides are reduced to nitrogen by using sufficient fuel to consume all the oxygen. With the non-selective abatement, some CO is formed and released to the atmosphere when using carbon containing fuels (104).

Methane and hydrogen are typically used as fuels for the reduction. The reactions which take place with methane are:

$$CH_4 + 4NO_2 \longrightarrow 4NO + CO_2 + 2H_2O \qquad (1)$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad (2)$$

$$CH_4 + 4NO \longrightarrow 2N_2 + CO_2 + 2H_2O \qquad (3)$$

Similar equations apply to reduction with hydrogen but four moles of hydrogen are required to replace one mole of methane.

The reduction reactions are highly exothermic resulting in temperature rises of 230°F per % oxygen reduction using methane and 270°F per % oxygen reduction using hydrogen. With noble metal catalysts, minimum inlet temperatures to assure ignition are about 850°F for methane and 400°F for hydrogen. With a typical tail gas containing 0.15% NO_2, 0.15% NO, 3% O_2, and the balance N_2, outlet temperatures could be 1540°F with methane and 1290°F with hydrogen for complete oxygen burnout. These temperatures are higher than the 1200°F limit for the turboexpanders which are used for recovering energy from the tail gas. Thus, for the complete oxygen burnout required for NO_x abatement, two reactor stages with intercooling are required.

Most catalytic tail gas treatment units have been installed for decolorization and energy recovery. Decolorization results from the reduction of the reddish-brown NO_2 to NO and partial oxygen burnout in a single reactor stage. Limited data (692) indicate some reduction in NO_x, perhaps about 35%. Moreover, while the NO is slowly oxidized to NO_2 in the atmosphere, dispersion lowers peak ground concentrations of NO_2 significantly below the levels which would prevail without treatment.

Supported platinum and palladium catalysts are both used for decolorization and non-selective abatement. Minimum ignition temperatures are lower with palladium, while platinum will withstand higher temperatures. Some of the catalyst supports used include ceramic honeycomb, ceramic spheres or pellets, and woven Nichrome ribbon.

The literature mentions (692) investments of $1-2 per SCFM for tail gas treatment (about 40 to 80 thousand dollars for a 500 T/D plant). These numbers tend to be misleading, since they cover only catalyst and possibly the reactor, excluding installation, for single-stage decolorization and energy recovery. Investments for completely installed two-stage non-selective abators have been quoted at $10-15/SCFM of tail gas (131). Actual investments will vary for each installation. Decolorization will be less costly than non-selective abatement, and selective abatement should be intermediate in cost.

The economics of fuel selection is location dependent. In many locations, hydrogen and methane (natural gas) cost about the same in ¢/MCF, and since four times as much hydrogen is required, methane is the cheaper fuel. Sometimes purge hydrogen from ammonia synthesis is available at low cost, but the quantities available are usually inadequate for decolorizing all the tail gas.

Comparatively little information is available on the use of non-noble metal catalysts for non-selective NO reduction in tail gas. The use of nickel on alumina and silica (296) has been described for tail gas NO_x reduction with natural gas. In a separate reference (168), nearly complete reduction of nitric oxide by hydrogen has been claimed with 75% nickel oxide on alumina at temperatures of 550-750°F and space velocities in excess of 50,000 V/V/hr. Presumably, some of the catalyst systems researched for automotive use could be used for tail gas emission control. Table 13 lists some of the systems studied to date for automotive exhaust control and the results obtained.

Table 13

NO_x Reduction Catalysts Studied For Automotive Emissions Control

Investigator(s)	Reaction	Catalyst		Experimental Conditions				Poisons
		Type	Pre-Treat	Temp.	NO Conc.	Space Vel.	% Conv.	
Baker & Doerr (128)	$2NO+2CO — N_2+2CO_2$	Harshaw CuO-203 82 CuO·17 Cr_2O_3	Reduction	120-270 °C	1500 ppm 1% CO in N_2	8-36,000 $Hr.^{-1}$	10-100	No data
Roth & Doerr (302)	$2NO+2CO \xrightarrow{N_2} N_2+2CO_2$	$CuCr_2O_4$ $Ba·CuCr_2O_4$	Reduction	100-250 °C	400 ppm 6% CO in N_2	10,000 $Hr.^{-1}$	10-100	No data
Ayen & Peters (124)	$2NO+2H_2 \xrightarrow{N_2} N_2+2H_2O$ $2NO+5H_2 \xrightarrow{N_2} 2H_2O+2NH_3$	10% Cu 29% Zn 31% Chromia Cirdler G-50		375-425 °C	1 to 5%	7,000-10,000 $Hr.^{-1}$		No data
Sourirajan & Blumenthal (328)	$\left.\begin{array}{l}NO\\ \&\\ NO_2\end{array}\right\} + \begin{array}{c}CO\\ or\\ H_2\end{array} \rightarrow \begin{array}{c}N_2\\ NH_3\end{array}$	30 CuO·70 SiO_2	Reduction	100-500 °C	500-800	7,000-10,000 $Hr.^{-1}$	30-100	No data
F. R. Taylor (342)	$\left.\begin{array}{l}NO+CO\\ or\ H_2\end{array}\right\} \xrightarrow[N_2]{He} N_2$	Zinc Cu Chromite iron chromite Ba-Cu chromite copper chrome alumina		200-320 °C	400-600C ppm NO 6% CO	15,000-25,000 $Hr.^{-1}$	20-100	Limited Data
Brennan (143)	Presumably $2NO+2CO \rightarrow N_2+2CO_2$	Alkali & alkaline earth crystalline $SiO_2-Al_2O_3$	N_2	400-600 °C	1000		10-95	No data
Baker & Doerr (127)	$2NO+2CO \rightarrow N_2+2CO_2$	62 CuO·5 CO_2O_3 33 Al_2O_3	Catalyst in reduced state	850°F		10,000 V/V/Hr.	High	400 Hrs. on commercial leaded gasoline

The problem with these catalyst systems is that they lack the mechanical strength or stability needed for a commercially acceptable automotive exhaust control system.

For stationary combustion sources, NO_x emission control by non-selective reduction would be best carried out by running the combustion under substoichiometric air/fuel conditions. This in itself would reduce NO_x formation and emissions, as work at Esso Research with low excess air combustion has shown (150). CO formed under these conditions would be available for further reduction of the nitrogen oxides. Ryason and Harkins, who have studied such reduction (303) under simulated conditions, have shown that it can be used to remove sulfur oxides and nitrogen oxides simultaneously from combustion gas. Using a copper or alumina catalyst at space velocities of about 10,000 V/V/hr and temperatures of about 1000°F, nearly complete reduction of both SO_x and NO_x were obtained from a simulated combustion gas containing CO in slight excess of that needed for the reduction. The reaction of SO_2 with CO initially results in the formation of sulfur which could be condensed out of the gas. With excess CO, however, the sulfur reacts further to form COS. Thus, the CO concentration would be very important in such a process, and this means the air/fuel ratio for the combustion would have to be very closely controlled.

Table 14

Ryason & Harkins' Data (303) For Simultaneous Reduction of SO_2 and NO_x by Catalyzed Reaction With CO; Copper-on-Al_2O_3 Catalyst, 1000°F, Reactants in N_2

SO_2, %	CO, %	CO_2, %	NO_x, ppm	Residence Time, Sec	Percent Reduction SO_2	Apparent Percent Reduction NO_x
0.47	1.3	8	~125	0.57	98	78-100
0.47	1.3	8	~125	0.46	98	31-100
0.47	0.97	5.8	~160	0.57	95	100

5.2.2 Selective Catalytic Reduction

The selective reduction of NO would permit substantial decreases in reductant requirements since stack gases typically contain 10 to 50 times as much oxygen as nitrogen oxides. Although catalysts have been found (318,370) on whose surfaces the reaction of NO with CO or H_2 in the absence of oxygen is faster than the reaction of O_2 with CO or H_2, the presence of oxygen in the NO gas apparently changes the oxidation state of these catalyst surfaces, thereby destroying their activity for the NO reaction. Barring a major breakthrough in catalyst development, it would appear that a selective reduction process using CO, H2, or methane, etc., for NO control is unlikely.

A very interesting control approach, on the other hand, is the use of ammonia as a selective NO_x reductant. The ability of NH_3 to reduce NO has long been recognized. Neumann and Rose (269), while studying the catalytic oxidation of ammonia to nitric acid concluded that the nitrogen formed during oxidation was the result of ammonia reacting with nitric oxide. These researchers cite the work of Reinders and Cats (295) who also considered the nitrogen formed to be due to the reaction between ammonia and nitric oxide. Michailova (259) studied the kinetics of the reaction between ammonia and nitric oxide on the surface of a platinum filament. She found the reaction proceeded according to the stoichiometric equation: $6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O$ and the rate was independent of the pressure of NO and NH_3 but dependent on their ratio. Michailova concluded that the reaction proceeded between adjacently adsorbed molecules on the platinum surface and on this basis derived a rate equation:

$$\frac{d\ NO}{dt} = \frac{P_{NH_3}\ P_{NO}}{(\alpha P_{NH_3} + \beta P_{NO})^2}$$

where α and β are constants and P is reactant partial pressure.

Thermodynamically, the reactions between NO_x and NH_3 are very favorable.

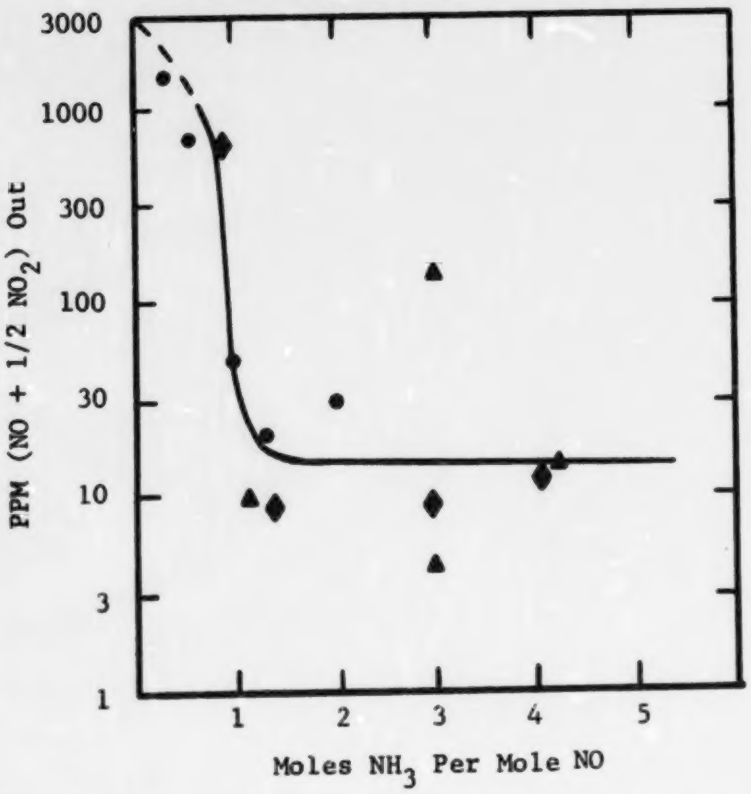
		ΔF-Kcal/g Mole NO_x @ 440°F
(4)	$6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O$	-73.2
(5)	$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$	-121.5

Reaction temperature must be generally controlled within the range of 400°F to 600°F, since ammonium nitrite is formed below 400°F and ammonia is oxidized to NO_x at higher temperatures. Since only the nitrogen oxides react, the energy available for recovery is small compared to the energy release in decolorization or nonselective abatement.

A control process using NH_3 with platinum group metal catalysts to reduce the NO emitted by nitric acid manufacturing processes is described by Cohn, Steele and Andersen (156). Andersen, Green and Steele (104) present data on the selectivity of NH_3 for reducing NO. These data are shown in Figure 1.

Figure 1

Selective Reduction of NO_x By Ammonia



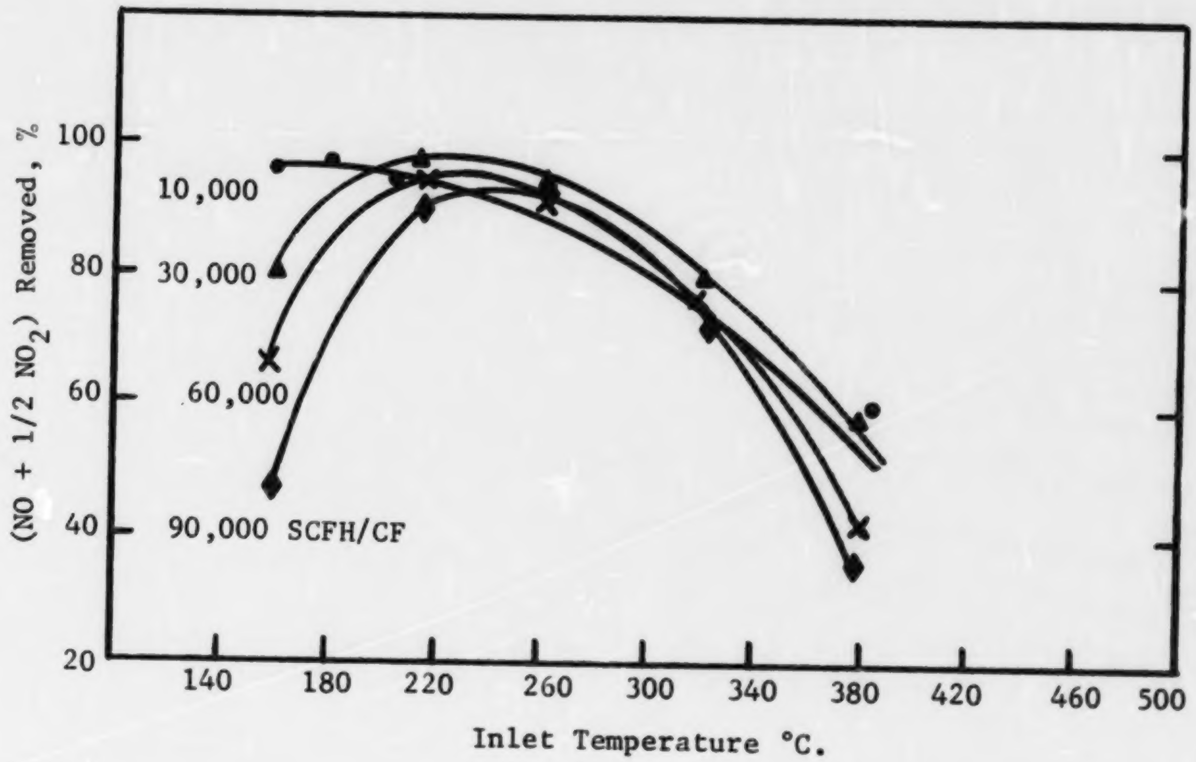
Catalyst, 0.5% Pt. on 1/2-inch Cylinders

	◆	▲	●
% NO	0.28	0.28	0.30
% O_2	3.4	3.4	3.0
% H_2O	0	1.6	0.66
% N_2	Balance	Balance	Balance
Catalyst volume, ml.	10	10	400
Inlet temp., °C.	149-166	149-166	163-180
Pressure, psig.	0	0	100

With the addition of only one mole of NH_3 per mole of nitric oxide, to a gas containing about ten moles of O_2 per mole of NH_3, the platinum catalyst used was sufficiently selective to reduce the NO concentration from 3000 to 30 ppm. Andersen, et al., also report the effect of temperature and space velocity on the completeness of the reaction. Their data are reproduced in Figure 2.

Figure 2

Effect of Space Velocity and Temperature on Ammonia Reduction of NO_x



Catalyst, 0.5% Pt on 1/3-in. cylinders, in 1.76 in. dia. reactor. 100 ml. catalyst used in 30,000-90,000 SCFH/CF experiments; 400 ml. for SCFH/CF.

Inlet gas: NO, 0.3%; O_2, 3.0; H_2O, 0.8; NH_3, 0.3. Pressure, 100 psig. Average temperature rise at and above optimum removal temperature, 33°C.

Although noble metal catalysts permit operating at very high space velocities, their use limits the applicability of this process in two ways. First, since platinum group catalysts are easily poisoned by sulfur, the use of these catalysts is restricted to gases containing less than 1 ppm of sulfur compounds (365). This means that the process cannot be used to control NO_x emissions from combustion of sulfur bearing fuels, even when used in conjunction with a flue gas desulfurization process, since no desulfurization process could be expected to reduce the sulfur content to such low levels. Second, the presence of NO_2 in the gas results in a loss of activity (104,111). This limits its use for nitric acid tail gas emission control, since about half the nitrogen oxides in these emissions are present as NO_2. To solve this second problem, it has been proposed that a two-stage process be used for nitric acid plant emission control. In the first stage, NO_2 would be reduced to NO by H_2, CO, or gaseous hydrocarbons while in the second stage, the NO would be reduced by NH_3 to nitrogen. The requirement to have two separate reductants in a two-stage process obviously complicates the process.

A much better approach to the NO_2 and the sulfur problem appears to be the use of non-noble metal catalysts that are less active than platinum but more tolerant to poisoning. A recent U.S. patent (271) claims the use of vanadium (V), molybdenum (VI) and tungsten (VI) oxides supported on alumina or silica to be effective catalysts for promoting the selective reaction of NH_3 with both NO and NO_2. Space velocities of 10,000 to 30,000 V/V/hr and temperatures ranging from 400° to 650°F are preferred. This patent also states that the vanadium oxide catalysts "are not sensitive to sulfur." Another patent (311), describing the use of a catalyst consisting of 85% Fe (III) oxide, 10% Cr (III) oxide and 2% Cr (VI) oxide on silica with alkali and alkaline earth promotion, also claims the ammonia reduction of nitrogen oxides in the presence of sulfur impurities. An example of a gas composition for which the catalyst is said to be effective is given in Table 15. These results, however, were obtained at a very low space velocity equivalent to about only 20 ft^3/hr/lb catalysts. Thus, this catalyst may not have been exposed to a sufficient volume of gas to see a sulfur poisoning effect.

Table 15

Gas Composition (311)

Component	Volume Percent
CO_2	6.0
O_2	8.0
N_2	86.0
SO_2	175 ppm
NO	120 ppm
NO_2	15 ppm

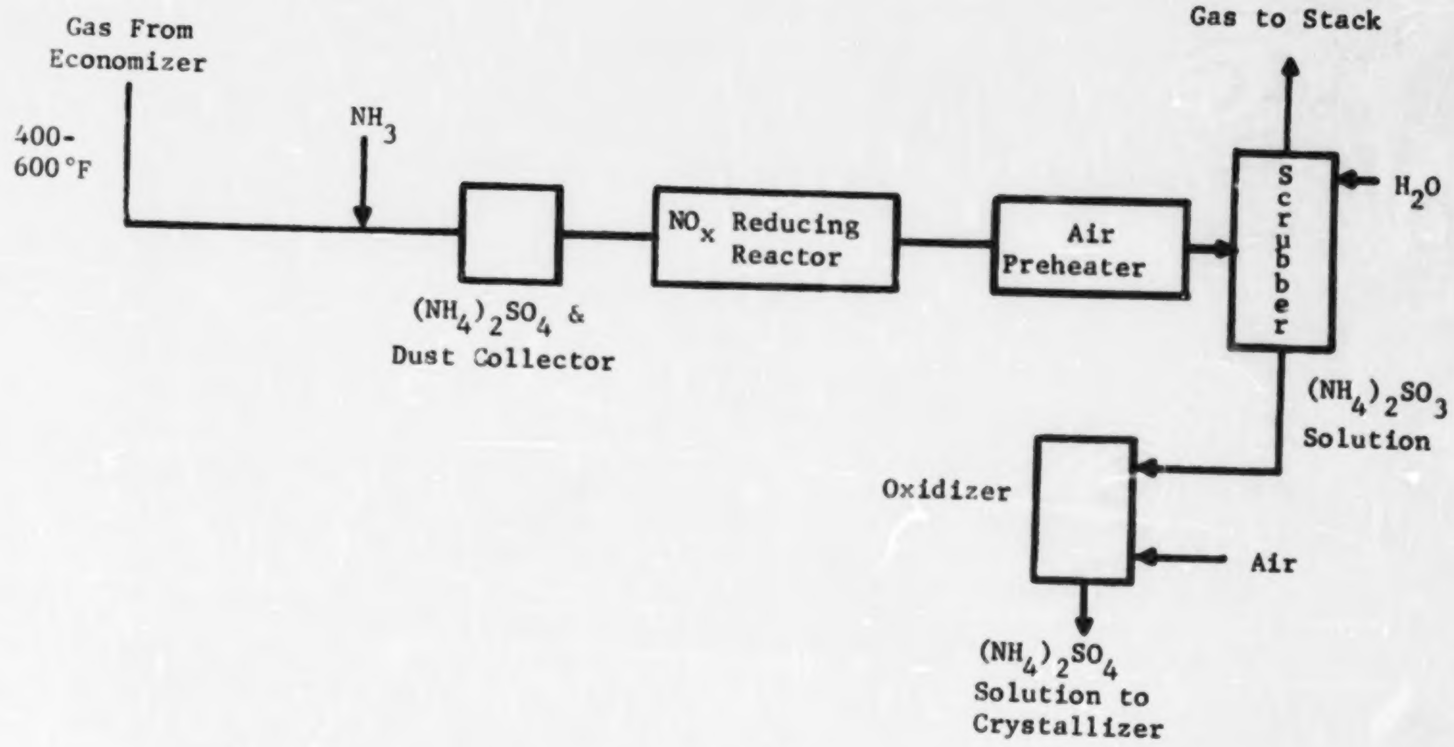
Andersen and Keith (107) claim the use of cobalt, nickel and iron containing catalysts for the ammonia reduction of nitrogen oxides. No mention of catalyst poisoning is made in their patent, but Anderson has said (365) that all of these catalysts were found to deactivate within a matter of hours or days when used with actual nitric acid plant tail gas.

The low temperatures at which the NO-NH_3 reaction can be catalyzed makes NH_3 reduction a potentially attractive method of controlling NO_x emissions from power plants. Low temperature reaction permits injecting the ammonia at the outlet of the boiler or air preheater. In fact, the surface of the air preheater itself could possibly serve to support the catalyst and become the reduction reactor. If a truly sulfur resistant catalyst exists or can be developed, the NH_3 reduction system could be used in coal and oil as well as gas-fired plants. The possibility would then exist of using NH_3 injection to control both the SO_x and NO_x emissions.

One example of a potential combined SO_x-NO_x control process is shown in Figure 3. In this process, sufficient NH_3 would be added to the flue gas to react with both oxides. NH_3 would first homogeneously react with the small amount of SO_3 present in the gas to form $(NH_4)_2SO_4$ which would be precipitated or filtered from the gas. Following the catalytic reduction of the nitric oxides, the gas would be scrubbed with water and the solution aerated to convert the ammonium sulfite solution to ammonium sulfate.

Figure 3

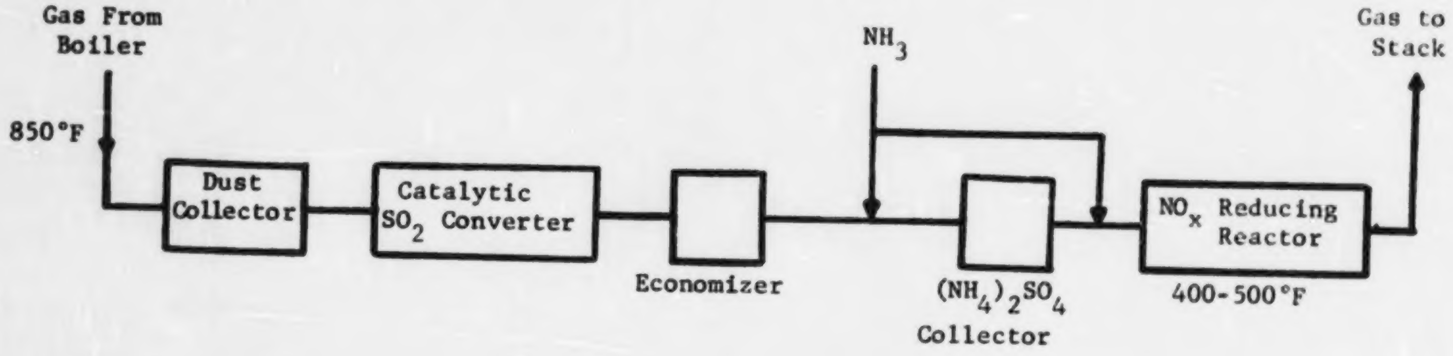
Potential Process for SO_x-NO_x Control with NH_3


Gas From Economizer
400-600 °F
NH_3
$(NH_4)_2SO_4$ & Dust Collector
NO_x Reducing Reactor
Air Preheater
Scrubber
H_2O
Gas to Stack
$(NH_4)_2SO_3$ Solution
Oxidizer
Air
$(NH_4)_2SO_4$ Solution to Crystallizer

If more complete desulfurization of the flue gas is required for the NO_x reduction, then an alternate processing scheme shown in Figure 4 might be used. Here, dust-free flue gas would first be oxidized as in the Kiyoura Process (324) to convert the SO_2 to SO_3. NH_3 injection would then remove most of the sulfur as $(NH_4)_2SO_4$ prior to reduction of the nitric oxides.

Figure 4

An Alternate SO_x-NO_x Control Process with NH_3


Gas From Boiler
850°F
Dust Collector
Catalytic SO_2 Converter
Economizer
NH_3
$(NH_4)_2SO_4$ Collector
NO_x Reducing Reactor
400-500°F
Gas to Stack

Besides NH_3, other reductants such as hydrazine or amines are reported (311) to be effective for reducing nitric oxides. These are more expensive than NH_3 and appear to offer no operating advantages. Urea, which is able to reduce nitrous acid (231) but not NO, is also more expensive.

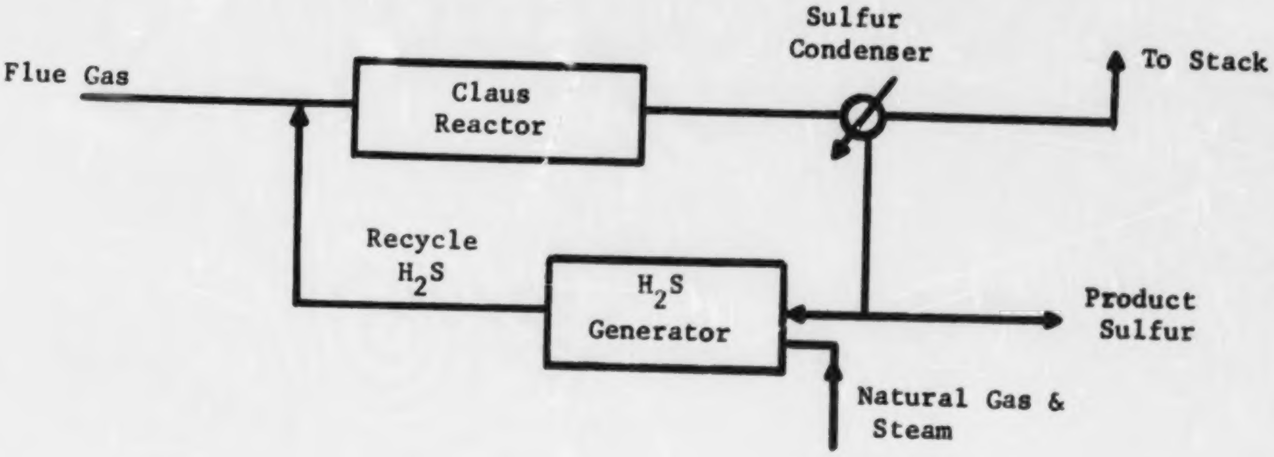
Another interesting possibility for a selective nitric oxide reductant is hydrogen sulfide. Hydrogen sulfide is able to reduce SO_2 selectively, and it is already being used in a flue gas desulfurization process currently being studied by Princeton Chemical Research under contract to NAPCA (343). This process uses the chemistry of the Claus Process:

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \qquad (6)$$

As shown in Figure 5, a concentrated H_2S stream produced by catalytically combusting natural gas with sulfur and steam is recycled in the Princeton Chemical Research process to the flue gas upstream of a Claus catalytic reactor. The proprietary catalyst used in the process selectively promotes the reaction of H_2S with SO_2 even though the flue gas contains an excess of oxygen. This selectivity enables recycling just enough H_2S for the SO_2 reaction. The reaction is carried out at a temperature of about 250 to 300°F.

Figure 5

Outline of Princeton Chemical Research SO_2 Control Process



Thermodynamically, the reaction of H_2S with NO is favored more than is its reaction with SO_2 and requires only half as much H_2S.

		ΔF Kcal/g Mole, 260°F
(7)	$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$	-17.4
(8)	$NO + H_2S \longrightarrow S + \frac{1}{2}N_2 + H_2O$	-65.1

The small amount of actual information available on this reaction is somewhat contradictory. Pierce (170) studied the gas phase reaction of H_2S with NO and found the reaction to proceed according to equation (8). He showed the reaction to be heterogeneous and catalyzed by both silica gel and glass wool. The reaction rate was found to have a negative temperature coefficient over the range of temperature 80 to 212°F, and this was ascribed to the decreased association of NO to N_2O_2 - the reactive specie. Dunnicliff, et al. (133), studying the same reaction in aqueous solution found it to be more complex, yielding ammonium thiosulfate, ammonium polysulfide, ammonium nitrite, sulfur, nitrous oxide and nitrogen.

Princeton Chemical Research plans in the near future to measure the effect of H_2S recycle on NO_x flue gas concentration (367). This should provide good indication of the potential of such a recycle process for the simultaneous control of SO_x and NO_x emissions.

5.3. ADSORPTION OF NITROGEN OXIDES

The adsorption of nitrogen oxides by solids provides another general approach to controlling NO_x emissions. A sizable number of solids have already been investigated for the adsorption of nitrogen oxides including silica gel, alumina, molecular sieves, char, manganese hydroxide and iron sulfide.

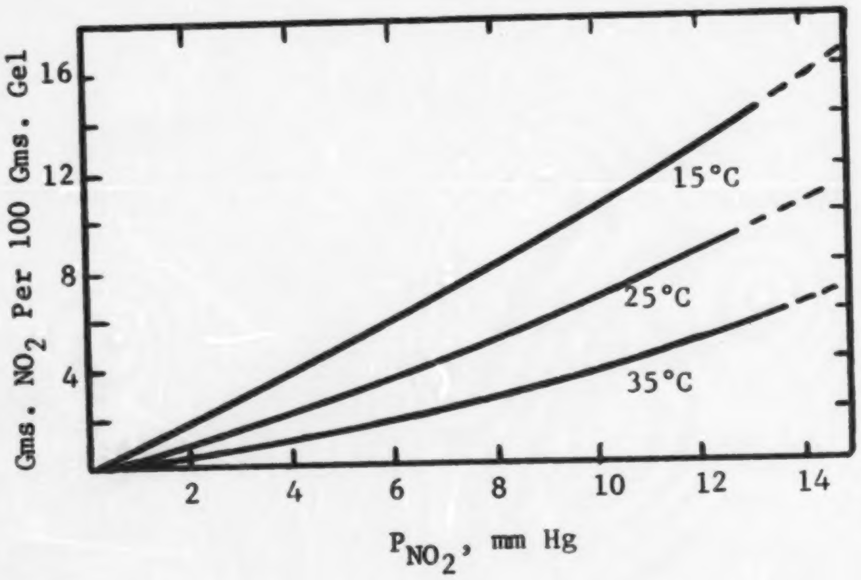
5.3.1 Silica Gel

Silica gel was studied extensively for recovery of the nitric oxide produced by the thermal fixation of nitrogen in the Wisconsin Process. Foster and Daniels, who directed the original work at the University of Wisconsin, reported (179) silica gel to have practically no adsorption capacity for NO as such. They also found that while dry silica gel was able to catalyze the oxidation of NO to NO_2 which could then be absorbed, moisture destroyed the catalytic activity. Furthermore, the silica gel was found to have a much higher sorption rate and capacity for moisture than for NO_2.

The capacity of silica gel for NO is not very impressive, even in the absence of moisture. Figure 6 shows the adsorption isotherms for the best of seven different silica gels screened by Foster and Daniels. The adsorption capacity can be noted to fall off sharply with increasing temperature.

Figure 6

Silica Gel Adsorption Capacity For NO_2



To achieve reasonable capacity with silica gel, the Wisconsin Process used three fixed beds to dry, oxidize NO, and then adsorb the NO_2 from refrigerated gas. The FMC Company (242,171) who took over the development of the process in 1946 evolved the idea of fluidized beds in place of cycling beds, thus permitting continuous operation. In FMC's version of the process, the NO-containing gas was dried to a dew point of about -60°F in the first fluidized bed of silica gel, oxidized to NO_2 in a second fixed bed of silica gel, and then cooled to 10°F and adsorbed in another fluidized bed of silica gel. Regeneration of this last bed at 400°F provided a gas containing about 80% NO_2.

The requirement to dry and cool the gas coupled with the low capacity of silica gel makes its use unattractive for removing dilute NO_x from stack gases. Table 16 gives the energy and silica gel requirements reported by Ermenc (171) for FMC's process where the NO level in the entering gas is one to two percent. This is three to six times more concentrated with respect to NO than is nitric acid tail gas, and 15 to 30 times more concentrated than is combustion flue gas. Process requirements and investment for such a process could be expected to vary about inversely with the NO concentration.

Table 16

Requirements for Wisconsin Process System

	Requirements/Ton of 100% HNO_3 Produced
Power	100 KWH
Water	2700 Gals.
Silica Gel	6 Lbs.
Investment	$50,000

5.3.2. Alumina

Both activated bauxite and alumina were reported by Levenson (240) to be better NO_x adsorbents than silica gel but to adsorb water preferentially as does silica gel. On the other hand, Berning, Cristian and Clarke (136) found that activated alumina is not as good an adsorbent as silica gel.

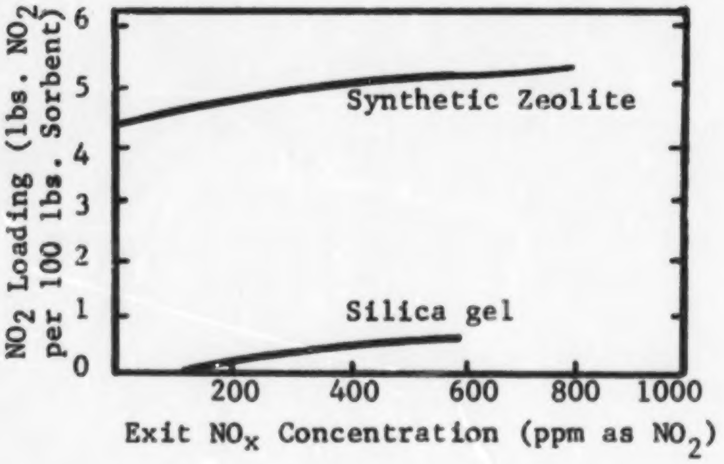
Although initial laboratory results by Saenz et al (304) indicated that a variation of the alkalized alumina process was capable of removing both sulfur dioxide and the oxides of nitrogen from flue gas, later results indicated this not to be the case. The only effect of the alkalized alumina appeared to be to catalyze the decomposition of NO_2 to NO.

Haseba, et al., (211) investigated the use of impregnated alumina adsorbents for removal of NO from coke oven gas. Of the 160 kinds of chemicals screened, they found that an adsorbent containing 5% $NaClO_2$ and 10-15% Na_2CO_3 supported on activated alumina worked best. The carbonate acted as a stabilizer for the $NaClO_2$ which by itself was not very effective for removing nitric oxides. With alumina, 100% removal of less than 1 ppm NO was possible until the $NaClO_2$ had been consumed in reaction with NO. Silica gel proved less effective as a carrier. The reaction of NO/NO_2 with the alumina-$NaClO_2$-Na_2CO_3 sorbent is reported (366) to be very fast, allowing 100% removal at space velocities as high as 10,000 V/V/hr and near room temperature. However, the use of alumina, impregnated with $NaClO_2$ or any other consumable oxidant would be impractical for NO_x emission control, since make-up costs for the oxidant would be high.

5.3.3. Molecular Sieves

The use of molecular sieves for treating nitric acid tail gas is reported by Sundaresan, Harding, May and Hendrickson (340). They compared the capacity of silica gel and molecular sieves with a dry gas and obtained the results shown in Figure 7. Concentrating on the molecular sieves, they ran a series of cycling experiments using actual nitric acid tail gas in which the nitric oxides concentration ranged from 1800 to 2500 ppm. Results are reported in Table 17. Regeneration was accomplished using either a hot air purge, or a combined steam/hot air purge. In either event, the nitric oxides were recovered partially as nitric acid and partially as NO_2, as seen in Table 17.

Figure 7



Adsorption Conditions

3.5% O_2

96.5% N_2

NO = Balance

Temp. = 75-95°F

Table 17

NO_x Removal in Zeolite Columns

(Plant tail gas for feed)

Cycle	Input Gas		Linear Veloc. Ft/Min	Space Veloc. Vol/Hr Vol	Mean Column Temp °F	Exit Concn. at End of Cycle	Lb NO_x Removed 100-Lb Bed		LB H_2O Removed 100-Lb Bed	
	Temp. °F	Psig					At 200 ppm Exit NO_x	End of Cycle	At 200 ppm Exit NO_x	End of Cycle
1	82	2.00	20.0	525	92	2400	5.75	6.69	8.26	9.95
2	78	2.00	20.0	525	85	1600	5.00	5.86	6.03	6.98
3	80	2.00	20.0	525	89	3200	3.80	4.44	5.66	7.60
4	84	7.50	51.0	1310	102	800	3.45	4.68	4.26	6.11
5	79	7.50	51.0	1310	94	1050	4.48	5.76	4.45	5.87
6	86	8.00	53.0	1370	102	1000	3.16	5.11	3.72	6.55
7	77	7.00	53.0	1370	95	700	4.96	5.58	5.23	6.16
8	77	2.10	27.0	675	92	300	4.24	4.96	4.39	5.21
9	82	2.80	27.0	675	95	200	4.42	4.42	4.43	4.43
10	94	5.50	48.0	1250	102	800	3.25	4.26	4.27	5.96
11	106	6.20	48.0	1250	109	1500	2.16	3.62	2.72	5.44

Table 18

NO_x Recovery from Zeolite Columns

Cycle	Total Input G. Moles	Method[a]	Recovery of NO_2 in Feed: As HNO_3 Acid Strength %	As HNO_3 G. Moles	As HNO_3 %	As NO_2 G. Moles	As NO_2 %	Total G. Moles	Total %
1	3.36	I	25.20	--	--	--	--	--	--
2	2.83	I	27.20	0.20	7.10	2.03	71.80	2.23	78.90
3	2.14	I	36.30	0.69	32.40	--	--	--	--
4	2.26	I	19.30	0.37	16.40	1.20	53.10	1.58	69.29
5	2.78	I	48.20	1.26	45.40	1.22	43.90	2.48	89.30
6	2.46	I	56.50	1.16	47.20	0.93	37.80	2.09	85.00
7	2.69	I	56.40	1.30	48.30	0.79	29.40	2.09	77.70
8	2.42	I	57.60	1.26	52.20	0.95	39.30	2.21	91.50
9	2.40	II	33.40	2.67	--	0.13	--	2.80	--
10	2.06	II	19.40	1.53	74.40	0.13	6.20	1.66	90.60
11	1.75	II	26.80	0.66	--	0.57	--	1.23	--

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[a] I = Heat plus air.
II = Heat plus steam plus air.

In a patent based on their work, Sundaresan, et al, (341) state that the molecular sieves catalyze the oxidation of NO to NO_2 and the subsequent reaction with water to nitric acid. Data are given in the patent for adsorption of SO_2 as well as NO_x by molecular sieves and also for co-adsorption of SO_x and NO_x. These data are shown in Table 19.

Table 19

Performance of and Synthetic Zeolite Systems

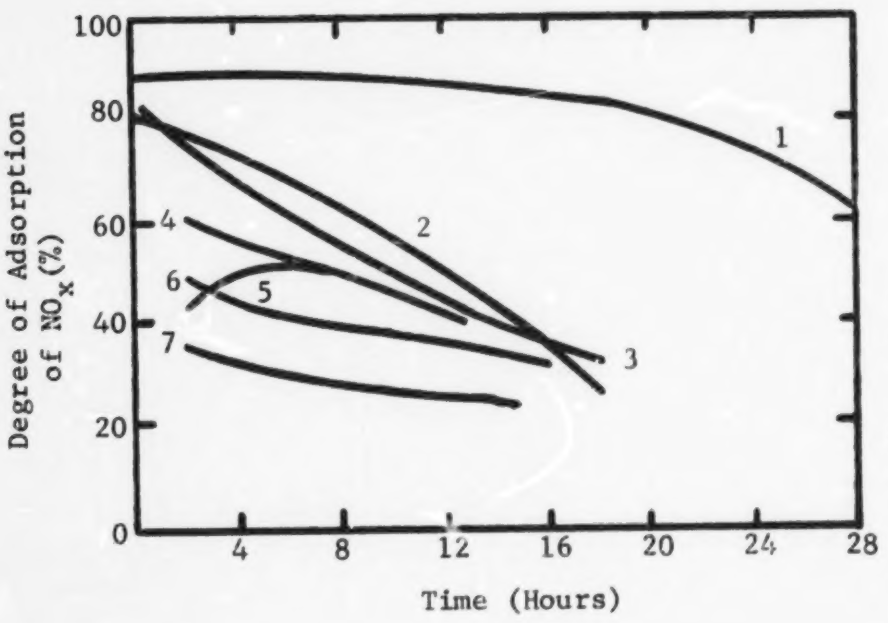
Synthetic Zeolite System, lb.	Volume of Gas Treated, ft^3	Cumulative Volume of Gas ft^3	Gas Concentration in Volume Percent				Loading, lb. of Oxides per 100 lb of Adsorbent	
			NO_x		SO_2			
			In	Out	In	Out	NO_x	SO_2
4.90	- - - -	0.00	0.247	0.000	- - -	- - -	- - -	- - -
	780.00	780.00	0.224	0.000	- - -	- - -	4.47	- - -
	140.00	920.00	0.221	0.020	- - -	- - -	5.00	- - -
	70.00	990.00	0.218	0.054	- - -	- - -	5.50	- - -
	190.00	1,180.00	0.214	0.214	- - -	- - -	5.86	- - -
0.69	- - - -	0.00	0.246	0.000	0.121	0.000	- - -	- - -
	40.00	40.00	0.282	0.024	0.121	0.000	1.74	1.15
	80.00	120.00	0.354	0.104	0.121	0.020	5.23	3.26
	136.00	256.00	0.354	0.354	0.120	0.076	8.16	3.87
0.69	- - - -	- - - -	- - - -	- - - -	0.182	0.000	- - -	- - -
	14.00	14.00	- - - -	- - - -	0.248	0.000	- - -	0.74
	16.00	30.00	- - - -	- - - -	0.320	0.020	- - -	1.80
	111.00	141.00	- - - -	- - - -	0.350	0.350	- - -	5.77

5.3.4. Char

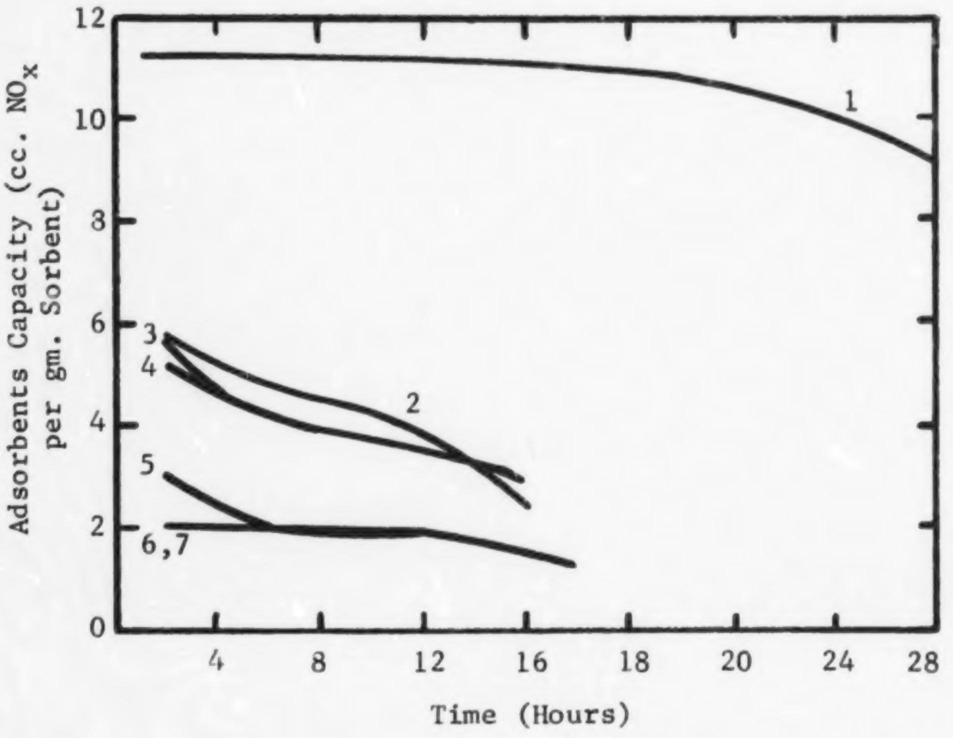
Char is also able to oxidize NO and adsorb it as NO_2. Ganz (190) in a study of adsorbents to control NO_x emissions from nitric acid manufacture found activated carbon to give a higher adsorption rate and capacity than silica gel, aluminum silicates, MnO_2, CuO or Hopcalite. The data of Figure 8 were obtained by Ganz with a gas containing .3% NO_x (60% NO, 40% NO_2) at a temperature of about 65°F and a space velocity of 1000 V/V/hr. Ganz found that complete desorption required temperatures on the order of 400°F to 650°F for the carbon and silica gel. At these temperatures, the carbon could be ignited and the silica gel crumbled. This led him to conclude that the aluminum silicates were the best NO_x adsorbents.

Figure 8

Capacity of NO_x Adsorbents (190)



Sorbents: 1) activated carbon, 2) aluminosilicate, 3) silica gel, 4) MnO_2, 5) hopcalite at SV= 1000 $m^3/m^3 \cdot$hour, 6) CuO, 7) hopcalite at SV= 1600 $m^3/m^3 \cdot$hour.



Feustel et al. (175) in a patent assigned to the Reinluft Gesellschaft-Essen, Germany, claims the use of charcoal, peat, semi-coke and other char materials for the removal of both sulfur and nitrogen oxides from stack gases (i.e., as SO_3 and NO_2). Unlike the silica gel, the presence of water vapor in the gas increases the capacity of the above sorbents through the formation of H_2SO_4 and HNO_3. According to the claims of the patent, the adsorbed oxides are recovered by heating the carbonaceous material to temperatures ranging between 600 and 1100°F, where the adsorbed oxides are reduced and desorbed.

$$\begin{array}{lcll} \underline{\text{Adsorbed}} & & \underline{\text{Desorbed}} & \\ 2SO_3 + C & \longrightarrow & 2SO_2 + CO_2 & (9) \\ 2NO_2 + C & \longrightarrow & 2NO + CO_2 & (10) \end{array}$$

Haagen-Smit (208) found the breakthrough capacity of char for nitric oxides to be about 5% that of SO_2 with powerplant flue gas. Since the Reinluft process designed for SO_2 control is already very expensive (140), a similar process for NO_x alone or for both NO_x and SO_2 would be even more expensive. Furthermore, the use of chars as adsorbents for NO_x removal may constitute a potential fire or explosion hazard.

5.3.5. Metal Oxides

The possibility of using metal oxides for adsorption of NO_x or co-adsorption of both NO_x and SO_x appears more attractive than the use of char. The use of manganese hydroxide as an adsorbent for nitric oxides was investigated by Purtseladse, et al. (290). Their investigation was more extensive than that of Ganz (190). Using relatively low space velocities (i.e., 350 V/V/hr) and temperatures of about 75°F, they found that hydroxide could remove a high proportion of the nitrogen oxides when the NO_2/NO ratio was one or more. Ganz on the other hand used MnO_2, and a NO_2/NO ratio of .67. Purtseladse et al. claim that the manganese hydroxide can be easily regenerated from the manganese nitrates formed by treatment with aqueous ammonia. Interestingly enough, the manganese oxides and

$$Mn(NO_3)_2 + 2NH_4OH \longrightarrow Mn(OH)_2 + 2NH_4NO_3 \qquad (11)$$

dioxides used in the Mitsubishi DAP-Mn Process for desulfurizing flue gas are also regenerated in this manner.

$$MnSO_4 + 2NH_4OH \longrightarrow Mn(OH)_2 + (NH_4)_2SO_4 \qquad (12))$$

Adsorbents other than manganese hydroxide or manganese dioxide may also prove useful for NO_x control. Barnes (131) showed that dry alkali and alkaline earth hydroxides are able to react with NO, but the reactions of all but cesium and rubidium hydroxides are too slow. (See Table 22) Ganz (Figure 8) showed a reaction between nitrogen oxides and copper oxide, and Walling's data (Section 5.1) suggest chemisorption of NO on NiO and Co_3O_4.

5.3.6. Metal Sulfides

Jordan, Ward, and Fulweiler (227) studied the adsorption of NO by more than 30 metal sulfides for purifying coke oven gas. Using pure nitric oxide, they obtained the results shown in Table 20 for sulfides with and without alkali.

Alkalized iron sulfides gave the best results, forming compounds similar to the Roussin complex salts $K[Fe_4(NO)_7S_3]$. Such complexes are unstable in oxidizing atmospheres and at all but low temperatures. Therefore, the use of these adsorbents is of questionable value for control of stack gas NO_x emissions.

Table 20

Adsorption* of NO By Metal Sulfides With and Without Alkali

Sulfide	Adsorption of Dry Substance or Mixture, Per Cent by Weight	
	Without Alkali	With 50% Alkali
Iron	--	20.6 ($CaCO_2$)
Iron	--	32.9 (Na_2CO_3)
Iron	10.9	27.1 ($NaHCO_2$)
Iron (ferrous)	13.4	11.3
Cobalt (ous)	6.8	17.9
Nickel (ous)	19.2	6.7
Manganese (ous)	0.51	2.4
Tungsten (sulfided tungstic anhydride)	0.33	3.2
Molybdenum (sulfided molybdenum sesquioxide)	1.7	1.4
Molybdenum (sulfided molybdic acid)	0.28	5.5
Arsenic (ous)	Nil	0.05
Arsenic (di-)	0.13	0.16
Antimony (ous, red)	0.25	3.6
Antimony (ous, black)	0.12	0.02
Antimony (penta-)	0.23	0.93
Bismuth	0.77	1.6
Tin (ous, hydrosulfide)	1.0	1.5
Tin (ous)	0.52	2.0
Tin (ic)	2.4	1.9
Lead	0.34	0.87
Aluminum	Nil	--
Magnesium	0.53	--
Strontium	4.3	--
Barium	5.6	2.6 (Na_2CO_3)
Calcium	3.2	--
Mercury (ous)	0.09	1.7
Mercury (ic)	0.15	1.5
Cadmium	0.53	3.3
Zinc	0.39	1.7
Silver	0.38	1.5
Copper (ous)	0.51	2.5
Copper (ic)	0.48	3.3
Sodium (di-, sulfided Na_2CO_3)	0.49	--
Sodium (hydro-, sulfided moist Na_2CO_3)	2.2	--

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* Pure NO passed through tube containing adsorbent at ambient temperatures for five hours.

5.4. ABSORPTION OF NITROGEN OXIDES

Absorption is the removal of a gas by a liquid as a result of its reaction with or its solubility in the liquid. Nitrogen oxides are absorbed by a large number of liquids, as Table 21 shows.

Table 21

Absorption of Nitrogen Oxides By:

- Water

$H_2O + NO \longrightarrow$ No Reaction

$H_2O + N_2O_3\ (NO + NO_2) \longrightarrow 2HNO_2$

$H_2O + 3NO_2 \longrightarrow 2HNO_3 + NO$

- Hydroxide and Carbonate Solutions

$2MOH + NO \longrightarrow$ No Reaction

$2MOH + N_2O_3\ (NO + NO_2) \longrightarrow 2MNO_2 + H_2O$

$2MOH + 2NO_2 \longrightarrow MNO_2 + MNO_3 + H_2O$

$M_2CO_3 + NO \longrightarrow$ No Reaction

$M_2CO_3 + N_2O_3\ (NO + NO_2) \longrightarrow 2MNO_2 + CO_2$

$M_2CO_3 + 2NO_2 \longrightarrow MNO_2 + MNO_3 + CO_2$

$M = Na^+, K^+, NH_4{}^+, Ca^{++}$, etc.

- Molten Alkali Carbonates or Hydroxides

$M_2CO_3 + 2NO_2 \longrightarrow MNO_2 + MNO_3 + CO_2$

- Sulfuric Acid

$H_2SO_4 + NO \longrightarrow H_2SO_4 \cdot NO$

$2H_2SO_4 + N_2O_3\ (NO + NO_2) \longrightarrow 2NOHSO_4 + H_2O$

- Solutions of Complex Forming Salts
- Organic Solutions

5.4.1 Aqueous Alkaline Solutions

Nitric oxide does not itself appreciably combine with water or basic solutions. Absorption in these cases requires that at least part of the NO be oxidized to NO_2, and complete removal requires that half of it be so oxidized. More complete oxidation does not appear to be needed, and may in fact be undesirable. Sherwood and Pigford (319) citing data of Eagleton, Langer and Pigford showed that at a 1% concentration of total nitrogen oxides in the gas, a 46% NaOH solution absorbed nitrogen oxides from a gas containing equal molar quantities of NO and NO_2 as much as ten times faster than NO_2 alone. When they compared the NO + NO_2 absorption rates with the calculated equilibrium concentrations of N_2O_3($NO + NO_2 = N_2O_3$), it was found that the rate was approximately proportional to the first power of the N_2O_3 concentration indicating it to be the reacting specie. Ganz and coworkers (184,185,189) studying the absorption of nitrogen oxides by solutions of $Ca(OH)_2$ and Na_2CO_3 also found that equal molar mixtures of NO and NO_2 were as easily or more easily absorbed than NO_2 alone. Ganz cites other Russian workers (183) who found the rate of absorption of equal molar mixtures of NO and NO_2 in alkali and sulfuric acid to exceed the rate of absorption of NO_2 alone. Koval and Peters (236) studying the effect of NO addition on the reaction of NO_2 with water found that the NO is absorbed along with the NO_2 to form nitrous acid and that the removal rate of nitrogen dioxide is only slightly changed by the addition. They developed two rate equations to account for the behavior observed:

$$\frac{-dNO_2}{dt} = k_1 (NO_2)^2 + k_2 (NO)(NO_2) - k_3 (HNO_2)^2$$

$$\frac{-d(NO)}{dt} = k_2' (NO)(NO_2) - k_3' (HNO_2)^2$$

where: k_1, k_2, k_2', k_3 and k_3' are rate constants.

An examination of the second equation shows that the absorption of NO will not take place when there is no NO_2 present and that in a basic solution (i.e., HNO_2 is zero), the rate of disappearance of NO will be a maximum when half the NO is oxidized to NO_2 and that when less than half the nitrogen oxides are present as the higher oxide, absorption provides less than complete nitrogen oxides removal. This is borne out by actual data. Thus, Combustion Engineering (284) and Universal Oil Products (285) both report about 20% nitrogen oxides removal in their caustic scrubbing desulfurization processes. Such a low removal would be expected on the basis that about 10% of the nitrogen oxides present in flue gas are in the form of nitrogen dioxide.

Chambers and Sherwood (151), in apparent contradiction to the above equations, found that NaOH solutions showed lower rates of absorption for NO_2 than did pure water. Streight (338) and Atsukawa, et al. (118), concluded, on the other hand, that the most promising method of absorbing nitrogen oxides was to use alkali solutions. Streight, Atsukawa and Ganz (184,185,189) give data on nitric oxide absorption rates in these solutions. Based on Streight's data, an actual control system was built by Dupont to remove nitrogen oxides from the effluent gases of a nitric acid and nylon intermediates plant. Although a caustic soda liquor proved satisfactory in this system, it was found that the operating costs could be substantially reduced by using an available water-ammonia-caustic soda solution (0.5% NaOH, 45% Na_2CO_3, and 0.03-0.5% NH_3).

5.4.2 Molten Alkali Metal Carbonates and Hydroxides

Molten alkali carbonates apparently react with NO_2 in the same way as do their aqueous solutions. North American Rockwell (Atomics International Division), in their initial studies (117) to define the potential of their molten carbonate stack gas desulfurization process found that NO_2 is absorbed by the melt to form nitrites and nitrates but NO is not absorbed unless it is first oxidized to NO_2.

With good contacting, Atomics International was able to obtain 90% removal of NO_2 at about 800°F from a gas containing 6% NO_2 and 94% He. Preliminary results indicated that the absorption reaction is first order with respect to the NO_2 concentration. With a gas containing 7.5% NO, 25% O_2 and 67.5% He, about 60% of the initial NO was absorbed.

At the lower concentration at which NO is found in stack gas (Table 4), oxidation may be too slow in a molten alkali scrubber. If so, the amount of absorption would be small. Furthermore, with SO_2 in the gas, the NO_2 formed would be at least partially reduced back to NO by reaction with SO_2 and molten sulfites.

$$NO_2 + SO_2 \longrightarrow NO + SO_3 \qquad (13)$$

$$NO_2 + M_2SO_3 \longrightarrow NO + M_2SO_4 \qquad (14)$$

The molten carbonate used to scrub the SO_2 in the Atomics International process is a eutectic of lithium, sodium and potassium carbonates in about equal proportions by weight. Barnes (131) has shown that anhydrous alkali and alkaline earth hydroxides can react with NO as follows:

$$4NO + 2MOH \longrightarrow N_2O + 2MNO_2 + H_2O \qquad (15)$$

$$6NO + 4MOH \longrightarrow N_2 + 4MNO_2 + 2H_2O \qquad (16)$$

(M = Li, Na, K, Rb, Cs, Ca, Sr, and Ba)

Using pure NO, Barnes found that the rates of these reactions increased with the atomic weight of the element. At room temperature, for example, he found that the complete reaction required several years with LiOH, several months with NaOH, several days with KOH and several hours with RbOH and CsOH. CsOH appeared to be the most reactive, yielding the results shown in Table 22.

Table 22

Reaction of CsOH with NO (131)

Contact Period	Temp., °C	Composition of Resulting Gas, Mole % N_2O	N_2
40 sec.	260	33	67
1 min.	290	29	71
10 min.	290	27	73
30 min.	290	21	79

By including CsOH (or carbonate) into their molten salt mixture, it may thus be possible for North American Rockwell to remove nitric oxide directly with their process. The N_2O produced would be less stable at the 800 to 900°F temperature at which the carbonates are maintained than at the 500°F temperature, and hence greater conversion to nitrogen should result. Furthermore, N_2O is not a pollutant so that venting N_2O to the atmosphere should present no problem.

5.4.3 Sulfuric Acid

The ability of strong sulfuric acid solution to absorb nitric oxides has long been recognized and is an integral step of the Lead Chamber Process for producing sulfuric acid (234). Two nitrogen oxide-sulfuric acid compounds are formed in this process - violet acid $H_2SO_4 \cdot NO$, and nitrosyl sulfuric acid $NOHSO_4$. In the former, the NO is only loosely bound to the sulfuric acid. Nitrosyl sulfuric acid is very stable in concentrated acid but becomes less so with increasing dilution. The nitrosyl sulfuric acid is formed by reacting equal molar quantities of NO and NO_2 with acid: $NO + NO_2 + 2H_2SO_4 \rightleftharpoons 2NOHSO_4 + H_2O$. Since sulfuric acid is such an effective dehydrating agent, moisture present in the gas that is scrubbed remains with the acid and promotes the reverse reaction. As Table 4 shows, combustion flue gas contains 40 to 100 times as much moisture as nitrogen oxides. A sulfuric acid NO_x flue gas scrubbing process must therefore have provision for reconcentrating the acid by removing this water. This would also be true if sulfuric acid were used to scrub nitric acid tail gas, but in this case the moisture content of the gas is much lower.

Under contract to NAPCA, Tyco Laboratories are studying a modification of the Lead Chamber Process for control of both nitrogen and sulfuric oxides emissions from power plants (309). A schematic of their process is shown in Section 5.5.2. To achieve the optimum 1:1 NO_2 to NO ratio and to oxidize the SO_2 to SO_3, the Tyco Process recycles NO_2 back to the flue gas. The SO_3 and NO_2 + NO are then absorbed in 80% sulfuric acid. In separate steps, the nitrogen oxides are stripped from the acid, which is concentrated and returned to the absorber. The stripped nitric oxides are scrubbed to remove NO_2 as nitric acid,with the remaining nitric oxides being oxidized to NO_2 for recycle to the flue gas. The data obtained by Tyco Laboratories prove that a sulfuric acid-NO_x absorption process is technically feasible. However, the thermal requirements for decomposing the nitrosyl complex and reconcentrating the sulfuric acid are so large that the economics of this process may not be favorable.

5.4.4 Complex Forming Salts

Nitric oxide is known to form complexes with a large number of compounds. Probably the best known of these are the ferrous sulfate and chloride complexes whose brown colors are the basis for nitrite and nitrate identification in the well known ring test. Excellent reviews of the nitrosyl complexes are provided by Moeller (261) and Addison and Lewis (100). Moeller classified the nitrosyl complexes into the six types shown in Table 23.

Table 23

Nitrosyl Complexes

Type of Complex	Examples
1 Nitrosyl Carbonyls	$Co(NO)(CO)_3$, $Fe(NO)_2(CO)_2$
2 $M^{I}(NO)_x A_y$ Complexes	
- Metal Nitrosyl Hydroxides	$Ni(NO)OH$
- Metal Nitrosyl Halides	$Fe_2(NO)_4I_3$, $Fe(NO)_2I$ $Fe(NO)I$, $Fe(NO)_3Cl$, $Co(NO)_2$ X $Ni(NO)X$ X=Cl,Br,I
- Metal Nitrosyl Thio Compounds	$M[Fe(NO)_2S]$ $M=Na^+$, K^+, NH_4^+ $M[Fe(NO)SSO_3]$ $M=Na^+,K^+,NH_4^+$ $[Co(NO)_2(SSO_3)_2]^{-3}$ $[Ni(NO)_2SSO_3)_2]^{-3}$
3 $M^{II}(NO)_xA_y$ Complexes	$Fe(NO)HPO_4$, $Fe(NO)SeO_4 \cdot H_2O$ $Pd(NO)_2Cl_2$ $Pd(NO)_2SO_4$
4 $M^{III}(NO)_xA_y$ Complexes	$Fe_2(NO)_2(SO_4)_3$ $B(NO)F_3$, $B(NO)Cl_3$

Type of Complex	Examples
5 $[MA_5(NO)]^{\pm}$ Complex Groups	$[Mn(CN)_5(NO)]^{-3}$ $[Fe(CN)_5(NO)]^{-2}$ $[Ru(CN)_5)(NO)]^{-2}$ $[Co(NH_3)_5(NO)]^{+2}$ $[Ni(NH_3)_5(NO)]^{+1}$ $[RuCl_5(NO)]^{-2}$
6 Miscellaneous Nitrosyl Complexes	$M_2SO_3 \cdot 2NO$ $M[Fe_4(NO)_7S_3]$ $M = Na^+, K^+$

where M is a cation, A is an anion of the complex.

In contrast to NO, few NO_2 complexes are formed. The best known NO_2 complex is $Co(NO_2)^=$ which can be precipitated as the potassium salt.

Little information is available on the use of complexing solutions to remove NO from gases. Gehlen (192) discusses the reaction of NO with alkali sulfites and hyposulfites (194) and a Linde patent (241) claim the use of alkali sulfite solution for removing NO from coke oven gas. Jordan, et al (227) claim, however, that such absorption was far too slow for practical use.

The most complete study to determine the NO complexing capacity and rate was made by Ganz and Mamon (183) for $FeSO_4$ solutions. They found that $FeSO_4$ and $FeCl_2$ solutions had capacities at least ten times greater than those of $CoSO_4$, $NiSO_4$, $CuCl_2$, and $MnCl_2$. $FeSO_4$ was chosen for more extensive study because it is less corrosive and more readily available than the chloride. The addition of small amounts of sulfuric acid (0.5 to 1.5%) was found to inhibit the oxidation of the ferrous salt, while not having much of an effect on the stability of the nitrosyl complex. Earlier work by Pound (286) had also shown the inhibiting effect sulfuric acid had on the oxidation of ferrous salts. Such inhibition is desirable since ferric solutions do not complex NO.

Using Ganz and Mamon's data (183), the amount of $FeSO_4$ solution needed to absorb the nitric oxides from a flue gas can be calculated. Based on the assumption that a 20% $FeSO_4$ solution is used and is continuously circulated between a NO absorbing tower at a temperature of about 140°F and a NO_x stripping tower maintained at a temperature of about 200°F, 15×10^6 gph are needed to remove seventy percent of the nitric oxide (at the 700 ppm level) from the flue gas of a 1000 MW power plant. The calculations assume no kinetic limitations, i.e., equilibrium saturation of the solution is achieved in the absorber. The very high solution circulation rates required by this system result from the low complexing capacity of the solutions. In an actual system, where there would also be kinetic limitations, even greater circulation rates would be required. Furthermore, Ganz and coworkers obtained their data in the absence of oxygen, CO_2, and SO_2. These might further lower the NO complexing capacity of the $FeSO_4$ solution.

5.4.5 Organic Solutions

Nitrogen oxides absorbing organic solutions could be used for scrubbing the stack gas provided they met certain criteria. An acceptable solution would have to have reasonable capacity for nitrogen oxides, would have to be stable to oxidation, must be very inexpensive or nearly totally regenerable, and must have low volatility. Low volatility is important for two reasons. First, evaporation losses from the scrubber must be made up, and second, solvent evaporation can change a NO_x pollution problem into an organic vapor pollution problem. An organic liquid having a vapor pressure of 500 μ at temperatures prevailing in the absorption tower (e.g., 120-150°F), for example, will produce a vapor emission of about 650 ppm in the stack gases - equivalent to a solvent loss of 4700 lb.-moles/day for a 1000 MW power plant and 150 lb.-moles/day for a 700 T/D nitric acid plant.

Amines, as a class, are able to form addition compounds with NO_2 and NO/NO_2 mixtures, but these reactions are not "clean" and the by-products are generally non-regenerable. At high temperatures, amines, like NH_3 act as reducing agents for nitrogen oxides (311). At low temperatures Lovejoy and Vasper (243) report that reaction of aliphatic and aromatic amines with N_2O_3 produce nitrosamine by-products in addition to the amine nitrite. Whereas the amine nitrite can be regenerated by treatment with a strong base or with steam,the nitrosamine cannot. Lovejoy and Vasper also found that diazonium nitrites were the principal products of reactions involving primary aromatic amines while aliphatic amines decomposed the N_2O_3 to nitrogen. In a NAPCA-sponsored study at A. D. Little (139) amines were also found to be degraded when used for SO_2 absorption and were judged unsatisfactory for use in a flue gas SO_2 scrubbing process.

Ganz and Mamon (183) evaluated amyl acetate, dimethylaniline, isoamyl alcohol, amyl ether and ethanol amine for NO absorption. They concluded that these compounds were of no practical value because of their low absorption ability (i.e., lower than $FeSO_4$ solutions).

Maury and Nahill (257) claim the use of aqueous solutions of electron donor solvents such as tri-n-butyl phosphate, dimethyl formamide, triethylene glycol, dimethyl ether, dimethyl sulfoxides, and hexamethyl phosphoramide for scrubbing nitrogen oxides and nitric acid vapor. For an equal molar mixture of NO and NO_2 at low partial pressures, they show the equilibrium absorption capacities of these solutions to be about 100 times that of water. Although these particular solvents are too volatile to be used for large scale scrubbing of gases, the possibility exists of synthesizing similar type higher molecular weight compounds with low vapor pressures. These could then be potential absorbents for nitrogen oxides.

It appears, in summary, that aqueous basic solutions, molten alkali and concentrated sulfuric acid offer the most potential as absorbents in a scrubbing system for removing nitrogen oxides from stack gases. Complexes forming solutions appear unattractive at this point of the study, but the types of organic solvents claimed by Maury and Nahill appear to warrant some additional consideration. These solvents, as well as concentrated sulfuric acid and the basic solutions appear to work best when 50% or more of the nitrogen oxides are present as NO_2. While this is approximately the case for nitric acid plant tail gas emissions (Table 4), NO predominates in combustion gas. Therefore, the nitrogen oxides must be oxidized before they can be scrubbed and this aspect is discussed in detail in Section 5.5 of this report.

With flue gas, the presence of SO_2 will increase the cost and complexity of a NO_x scrubbing process. This is so, first, because NO_2 is consumed and additional NO is formed in the very fast reaction between NO_2 and SO_2 (to form SO_3), and second, because the sulfur oxides will react with some absorbing solutions, decreasing their nitrogen oxide capacity and increasing the solution make-up requirements.

5.5 EQUIMOLAR NO-NO_2 SORPTION SYSTEMS

In the preceding sections of this report, it was pointed out that alkali solutions, concentrated sulfuric acid, and certain solid adsorbents were most effective in removing nitrogen oxides from gases where the nitrogen oxides were present in about equimolar concentrations of NO_2 and NO. While nitric acid plant emissions are about equally divided between NO and NO_2, nitrogen oxide emissions from combustion are predominantly NO. Thus, the use of these absorption or adsorption processes for controlling the nitrogen oxide produced in combustion requires a means of providing this equimolar mixture of NO and NO_2. This can be done in one of two ways. The first is by oxidizing half the NO contained in the flue gas; the second is by recycling NO_2 produced by regenerating the sorbent.

5.5.1 Partial Oxidation

Nitric oxide is oxidized by air (O_2) to nitrogen dioxide, but with low NO concentrations, the termolecular non-catalyzed reaction is very slow. Using published rate data (145), the residence time required for converting half of the 700 ppm NO found on the average in flue gas with the available flue gas oxygen (about 3%) is calculated to be about 33 minutes at a temperature of 120°F. At higher temperatures, this reaction is even slower, i.e., it is one of the few reactions that exhibits a negative temperature coefficient (115,362).

The reaction time can be decreased somewhat by injecting additional air into the flue gas to increase the O_2 concentration. Since such addition also lowers the NO concentration, and the the rate of oxidation varies with the square of the NO concentration (i.e., rate of oxidation = $k\,[NO]^2\,[O_2]$), there is an optimum dilution at about 30% air. At this optimum, the reaction time is calculated to be about 18 minutes, but this is still several orders of magnitude above what is practical for flue gas conversion.

Practical reaction times can be achieved using ozone as the oxidant. Based on published rate data (224), calculations show that half the NO could be oxidized in .0035 seconds using only 5% excess ozone. At a cost of about 15¢/lb, however, the cost of the ozone required in a power plant would be equal to about \$2/ton of coal burned. Furthermore, these costs assume the flue gas to be SO_2-free. If this is not the case, the ozone requirements would be even greater because of rapid competing reactions (13) and (17).

$$SO_2 + NO_2 \longrightarrow SO_3 + NO \qquad (13)$$

$$SO_2 + O_3 \longrightarrow SO_3 + O_2 \qquad (17)$$

The catalytic oxidation of NO has been studied by a number of investigators. Burdick (145) found charcoal to be the most effective NO oxidizing catalyst of the materials he tested--Table 24. Kircher and Hougen (232) found activated carbon to be more active and less sensitive to moisture than silica gel. Based on these findings, Chu and Hougen (154) used activated carbon as the catalyst on a paper design study of an optimized catalytic nitric oxide reactor.

Table 24

Activity of NO Oxidation Catalysts Evaluated (145)

Catalyst	Temp. °C	Gas Comp.[(a)] NO %	O_2 %	H_2O %	3rd Order Rate Constant k'[(b)]
Glass container	0	3.11	20.4	0.1	21
empty	25	2.91	20.4	0.1	11
Crushed glass	25	2.82	20.4	0.1	12
	50	3.45	20.3	0.1	15
Untreated pumice	25	2.97	20.4	0.1	13
Pumice impregnated					18
with tungstic acid	50	3.06	20.4	0.1	21
in HNO_3	50	3.20	20.3	0.1	18
with tungstic acid in soln. of hydrogen peroxide	25	3.04	20.4	0.1	17
with NiO	25	3.00	20.4	0.1	16
with CoO	25	2.86	20.4	0.1	15
with metallic Ni	25	3.07	20.4	0.1	19
with metallic Co	25	3.02	20.4	0.1	19
with MnO_2	25	2.98	20.4	0.1	15
Platinized pumice	25	2.97	20.4	0.1	17
Platinized asbestos	25	2.02	20.4	0.1	17
Coke	25	2.02	20.4	0.1	20
Common charcoal	25	2.98	20.4	0.1	19
Coconut charcoal	25	1.33	2.96	0.1	10,000
	25	1.39	2.96	0.1	12,000
	80	1.63	2.59	0.1	8,800
	25	1.87	2.94	1.0	1,400
	25	1.86	2.04	1.0	1,100
	25	1.77	2.94	1.0	930
	50	1.31	2.96	1.0	1,350
	80	1.96	2.90	1.0	2,650
Peach-kernel charcoal	80	1.87	2.90	1.0	2,010
	80	1.71	2.90	1.0	2,130
	80	1.23	2.79	5.7	2,710
	80	2.22	2.70	5.6	3,110
	55	1.79	2.66	5.8	1,590
	55	1.66	2.80	5.7	1,165
	53	1.51	2.78	5.7	808
	53	1.59	2.77	5.7	910
	53	1.66	2.78	5.7	765
	100	1.27	2.45	14.7	3,440
Steamed coke	80	2.63	2.81	3.9	329

Footnotes on next page.

(a) Mole %, balance N_2

(b) For differential form of rate eq. $-\frac{dC}{dt} = k(C')(C)^2$

Integrated form of rate eq. -

$$k't = \left[\frac{1}{2C'_i - C_i}\right]\left[\frac{1}{C} - \frac{1}{C_i}\right] - \frac{2.3}{(2C'_i - C_i)^2} \log_{10} \frac{(2C'_i - C_i + C)C_i}{2C'_i - C}$$

where C_i = initial conc. of NO, mole %

C = conc. of NO at time t, mole %

C'_i = initial conc. of O_2-mole %

C' = conc. of O_2 at time t, mole %

t = reaction time in seconds

k' = 1/2 k

Based on Burdick's data with a rate constant, k, of 3000 for peach-kernel charcoal (6% moisture in the gas), calculations show that half of the NO at a 700 ppm level can be oxidized in about 8 seconds. With SO_2 in the gas to consume NO_2 as it forms, even longer reaction times are needed. Thus, a "desulfurized flue gas" containing only 270 ppm SO_2 (90% removal of 2700 ppm), for example, would require a minimum calculated gas residence time of about 12 seconds assuming no decrease in catalyst activity due to the SO_2. Although this is more than a hundredfold decrease in reaction time compared to the 18 minutes required for the uncatalyzed reaction, it is still much too slow. Thus, for a 1000 MW power plant, about a 1.8×10^6 ft^3 char-filled reactor would be required to provide a contact time of 12 seconds.

5.5.2 NO_2 Recycle

The equimolar NO_2-NO ratio can be achieved by recycling NO_2 back to the flue gas - the recycle NO_2 being obtained from the spent sorbent used to remove the nitrogen oxides from the flue gas. In the case of alkali or caustic scrubbing, for example, the spent solution could be evaporated and the resulting nitrites thermally decomposed. Solid sorbents could be thermally regenerated in the same way, while nitrogen oxides absorbed by sulfuric acid could be stripped at higher temperatures from the acid. The nitrogen oxides, released in a concentrated form in the regenerator or stripper, could then be easily oxidized by air to NO_2. The reaction time and therefore the size of the reactor required for this oxidation would be much less than required for the direct oxidation of the dilute nitric oxide in flue gas.

For an SO_2-free gas, the amount of NO_2 recycled to the flue gas would be approximately equal to the amount of NO present (actually, somewhat less since there would already be some NO_2 present in the flue gas). With SO_2 in the gas, sufficient NO_2 would have to be provided, however, to oxidize essentially all the SO_2 to SO_3 and still provide enough to give the 1/1 NO_2-NO ratio. Since the oxidation of SO_2 by NO_2 produces additional NO by reaction 13, the requirements for NO_2 change sharply with the SO_2 level of the gas as shown in Table 25.

Table 25

Effect of Flue Gas Desulfurization on NO_2 Recycle Requirements

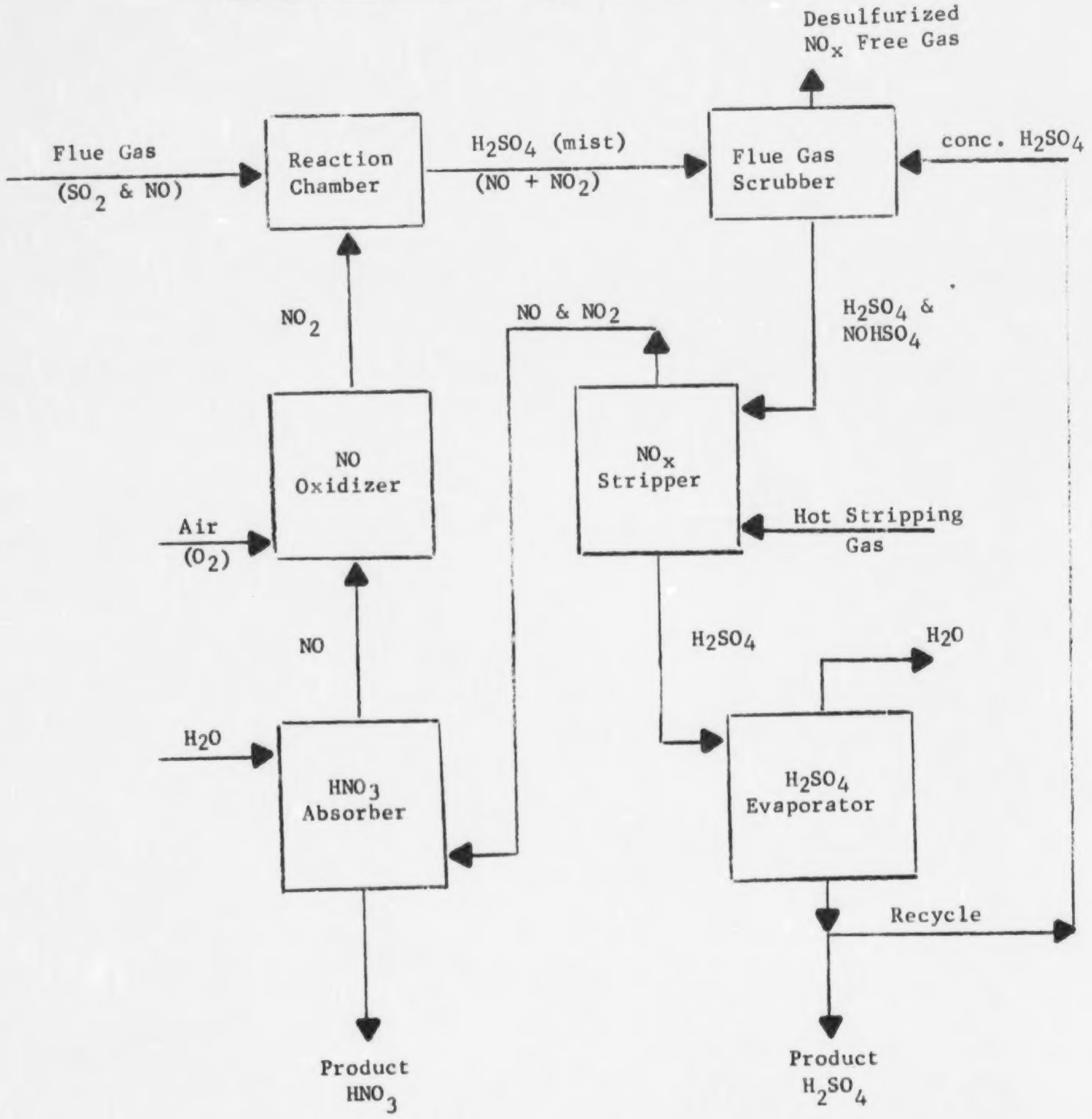
Basis: Flue Gas Containing 700 ppm NO and 2700 ppm of SO_2 (4% S Coal)

% Desulfurization	Moles NO_2 Injected per Mole of NO to Produce 1/1 NO/NO_2
100	1.00
90	1.77
75	2.93
50	4.85
25	6.80
0	8.70

Under contract to NAPCA, Tyco Laboratories (309) have been studying a NO_2 recycle system in which concentrated sulfuric acid serves as the absorbent for both the sulfur and nitrogen oxides. The Tyco Process, fashioned after the Chamber Sulfuric Acid Process, is shown outlined in Figure 9. The basic features of their process are: contacting the flue gas with sufficient NO_2 to oxidize the SO_2 to sulfuric acid mist and to produce an equimolar mixture of NO and NO_2; removing the acid mist and the nitrogen oxides with concentrated sulfuric acid; heating the acid to release the NO and NO_2 for partial conversion to nitric acid and for recycle to the SO_2 oxidation step; concentrating the diluted sulfuric acid; and recirculating part of it to the scrubber.

FIGURE 9

FLOW DIAGRAM FOR TYCO SO_2-CONTROL PROCESS


Desulfurized
NOx Free Gas
Flue Gas
(SO2 & NO)
Reaction Chamber
H2SO4 (mist)
(NO + NO2)
Flue Gas Scrubber
conc. H2SO4
NO2
NO & NO2
H2SO4 &
NOHSO4
NO Oxidizer
NOx Stripper
Air
(O2)
Hot Stripping Gas
NO
H2SO4
H2O
H2O
HNO3 Absorber
H2SO4 Evaporator
Recycle
Product
HNO3
Product
H2SO4

In the flue gas reactor: (18)

$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4(\text{mist}) + NO$

In the scrubber and NO_x stripper: (19)

$(NO_2{+}NO) + 2H_2SO_4 \underset{\text{stripper}}{\overset{\text{scrubber}}{\rightleftharpoons}} 2NOHSO_4 + H_2O$

In the HNO_3 absorber: (20)

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

In the NO oxidizer: (21)

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

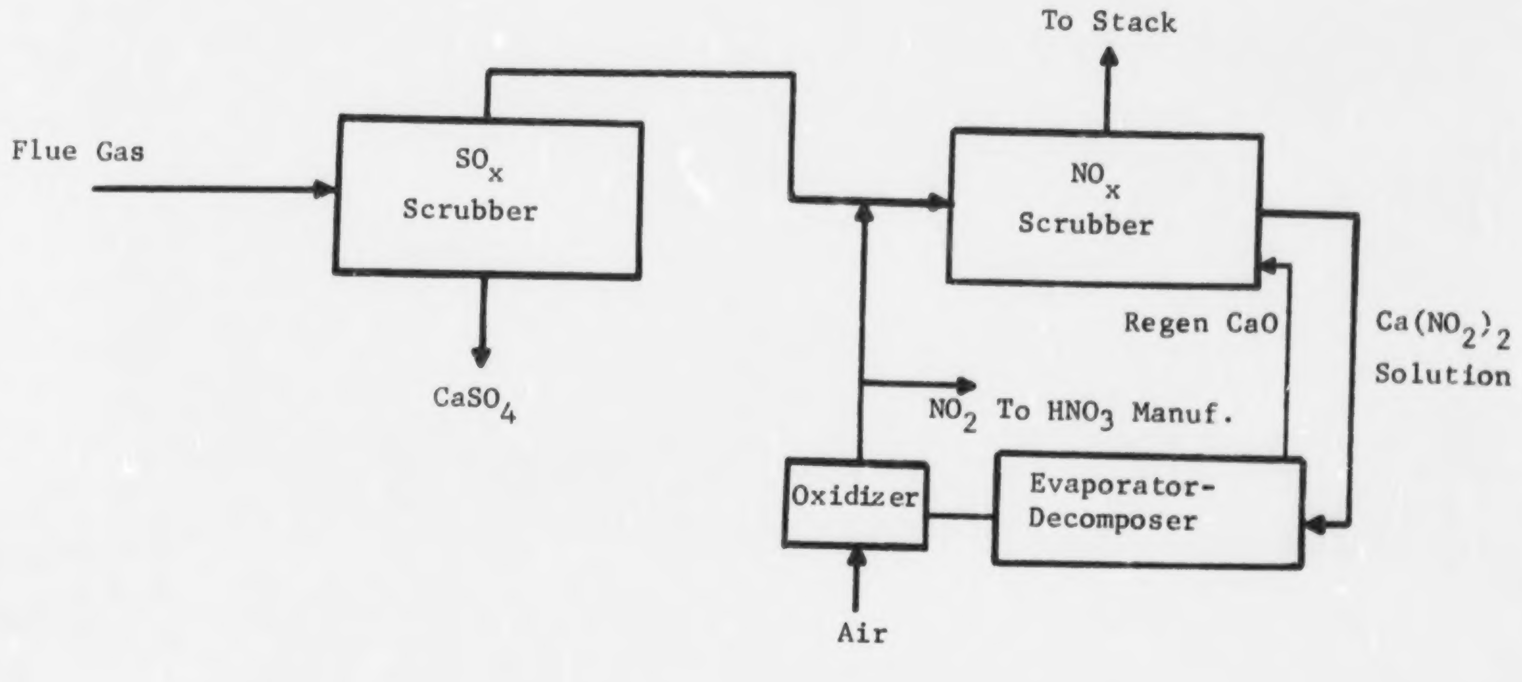
The major problem with the Tyco Process is that almost all of the combustion product water will be condensed in the concentrated sulfuric acid in the scrubber. The heat required to reconcentrate the acid and strip the nitrogen oxides, amounts to a large percentage of the total boiler heat rate. For a boiler fired by coal, fuel consumption for the control process would be about 20% that for the boiler, while for an oil fired boiler (i.e., more moisture in the flue gas), it would be about 30%.

These large thermal requirements can be reduced by substituting a caustic solution for sulfuric acid in the scrubber. Figure 10 shows the outline of a potential process using NO_2 recycle in conjunction with limewater scrubbing. Assuming such a system is operated with a 10 wt. % $Ca(NO_2)_2$ solution in the NO_x scrubber and that 90% desulfurization is achieved in the first scrubber, the thermal requirements for evaporating and decomposing the nitrites produced would be about a third of the total heat input to the Tyco Process.

Desulfurizing the flue gas up-stream of the nitrogen oxide scrubber is desired to minimize NO_2 recycle since the thermal requirements for the evaporation and decomposition vary in just about direct proportion to this recycle. Thus, with undesulfurized gas, the thermal requirements would be five times greater than with the desulfurized gas (eliminating the first scrubber).

FIGURE 10

POTENTIAL LIMEWATER SCRUBBING SYSTEM WITH NO_2 RECYCLE



A recycle system using a solid sorbent to control the emissions of either nitrogen oxides or both nitrogen and sulfur oxides could have even lower thermal requirements than the caustic scrubbing system. Using a solid sorbent which adsorbs little or no water vapor, the major thermal requirements for its regeneration would become the relatively small endothermic heat of desorption or decomposition. The manganese oxides are possible candidates for use in such a system. Manganese oxides react with SO_2 forming $MnSO_4$, and react with NO and NO_2 (290) forming $Mn(NO_3)_2$. The nitrate portion can be decomposed back to the oxide at a temperature of about 400°F liberating nitric oxides for oxidation and recycle. The sorbent could then be either reduced with liberation of SO_2, or treated with aqueous ammonia to convert the sulfite portion back to oxide with formation of ammonium sulfate.

6. NO_x EMISSION CONTROL BY COMBUSTION PROCESS MODIFICATION

The combustion of fossil fuels with air as the oxidant results in the formation of oxides of nitrogen. These species are formed by the direct combination of molecular nitrogen and oxygen in flames. Thus, in the combustion of natural gas which is virtually free of bound nitrogen, the quantities of NO_x produced (in excess of 1000 ppm NO_x in flue gases from some electric utility boilers, as discussed in Section 4) clearly indicate that high temperature fixation of atmospheric nitrogen occurs. In contrast, the formation of sulfur oxide pollutants is solely dependent on the sulfur content of the fuel.

Chemically bound nitrogen in the fuel can also contribute to the overall NO_x emission from combustion processes. Although the role of the fuel nitrogen content in NO_x emissions remains to be studied further, it is safe to conclude that in high temperature combustion processes, the elementary reactions between N_2 and O_2 play a major role in the formation of NO_x.

Under typical combustion conditions, the only oxide of nitrogen of any consequence is nitric oxide. Thermodynamic equilibrium highly favors the formation of NO over that of NO_2 at high temperatures (see Table 6). Once formed at high temperatures, the NO could react with excess oxygen to yield NO_2. Although this oxidation reaction has a negative temperature coefficient, the residence time usually available in combustion equipment is too short for an appreciable fraction (more than 5-10%) of the NO to be oxidized to NO_2. Thus the bulk of the NO_2, favored by the thermodynamic equilibrium under ambient conditions, is produced in the atmosphere, rather than within the confines of the combustion source.

The reaction leading to NO formation in fuel/air flames is

$$N_2 + O_2 \rightleftharpoons 2\,NO \qquad (22)$$

Experimental evidence in the literature indicates that NO formation occurs via a chain reaction involving N and O atoms, instead of the four-center process of equation (22). This chain reaction, first postulated by Zeldovich(675) to support his findings on NO formation in hydrogen-air combustion, has also been established for shock-tube reactions of N_2-O_2 mixtures, in the absence of any fuel(554). The chain mechanism can be represented as follows:

$$N_2 + O \rightleftharpoons NO + N \qquad (23)$$

$$NO + O \rightleftharpoons O_2 + N \qquad (24)$$

Oxygen atoms are supplied by the thermal dissociation of molecular oxygen:

$$O_2 + M \rightleftharpoons 2\ O + M \qquad (25)$$

Equilibrium is customarily assumed to hold for reaction (25). However, in fuel-air flames the oxygen atom concentration exceeds that calculated based on the equilibrium dissociation of oxygen. Therefore, the kinetics derived on the basis of the equilibrium assumption provide a lower limit for the rate of NO formation.

The rate of NO formation is very highly temperature dependent. Zeldovich estimated an activation energy of about 129 kcal/mole for NO formation. More recent data verify this order of magnitude (554) with a currently used value of 135 kcal/mole. The rate of formation of NO is given by the following expression derived on the basis of the chain mechanism of reactions (23)-(25):

$$\frac{d(NO)}{dt} = 3.0 \times 10^{14}\ e^{-135,000/RT}\ (N_2)(O_2)^{1/2} \qquad (26)$$

where concentration terms are given in g. moles/cc and the rate of NO formation is in units of g. moles/cc/sec.

The very high activation energy for NO formation is responsible for the extreme dependence of reaction rate on temperature. The homogeneous decomposition of NO back into N_2 and O_2 has a much lower, but still appreciable activation energy. A number of investigators have studied the NO decomposition reaction, and various estimates have been made for the kinetic parameters of this process. (546)(554)(672)(674) It appears that below 1100°K NO decomposition is heterogeneous, while above 1400°K it is strictly a homogeneous gas phase reaction. The question of whether a chain mechanism or the reverse of reaction (22) is the best representation of NO decomposition at flame temperatures is still unsettled. However, from the standpoint of practical applications, i.e., using combustion modifications to control NO_x emissions, the most important factor in the NO chemistry of flames is the rate of formation of NO.

In almost all cases the NO concentrations measured are below the values corresponding to equilibrium at peak flame temperatures. Therefore, in air/fuel combustion, control of NO_x emissions by combustion modification techniques must be based on factors affecting the kinetics of NO formation (a possible exception to this statement may be the development of low temperature combustion methods, such as fluidized bed or flameless surface combustion, where the thermodynamic equilibrium is in favor of low NO_x concentrations)

Since NO formation is so highly temperature dependent, the reduction in NO_x emission corresponding to relatively modest peak flame temperature reductions can be very significant. This is, of course, an oversimplification of the actual situation, in that not only the peak flame temperature, but the entire time-temperature history of the combustion process requires control. Nevertheless, relatively simple techniques (to be discussed later in this section) aimed at the reduction of peak flame temperatures have been successful in accomplishing reductions in NO_x emissions on the order of 50%, compared with "standard" operating practices.

The consequence of the kinetics of NO formation is that NO_x control by combustion process modification must consist of lowering flame temperature, limiting the availablity of the reactants, oxygen and nitrogen, or a combination of these factors. In practice, limiting the amount of available oxygen for NO formation may be simpler than eliminating nitrogen (unless combustion with oxygen enrichment can demonstrate favorable effects on NO_x emissions). As will be discussed later, low excess air operation has been used (on a limited basis) successfully for lowering NO_x emissions. The trade-off is between higher flame temperature and lower available oxygen concentration. As the excess air level is increased, the NO_x concentration must go through a maximum value. Further increase in excess air dilutes the flame to such an extent that NO formation is reduced because of lower peak temperatures.

Based on the potential simplicity of NO_x control via combustion modification, this area is regarded as the most promising method of controlling NO_x emissions. If successfully applied, the modification of design features or operating conditions could be the least expensive and most readily applicable technique of NO_x control for various types of combustion equipment. At least partial success has been found for NO_x reduction by a number of combustion modifications, which will be discussed below.

So far in this systems study, potential combustion process modification technology has been identified. In the studies to follow the period covered by the present report, the detailed analysis of variables and the examination of the applicability of this critical area will be carried out. Careful attention will be given to the area of combustion process modification techniques on the basis of both basic and practical considerations.

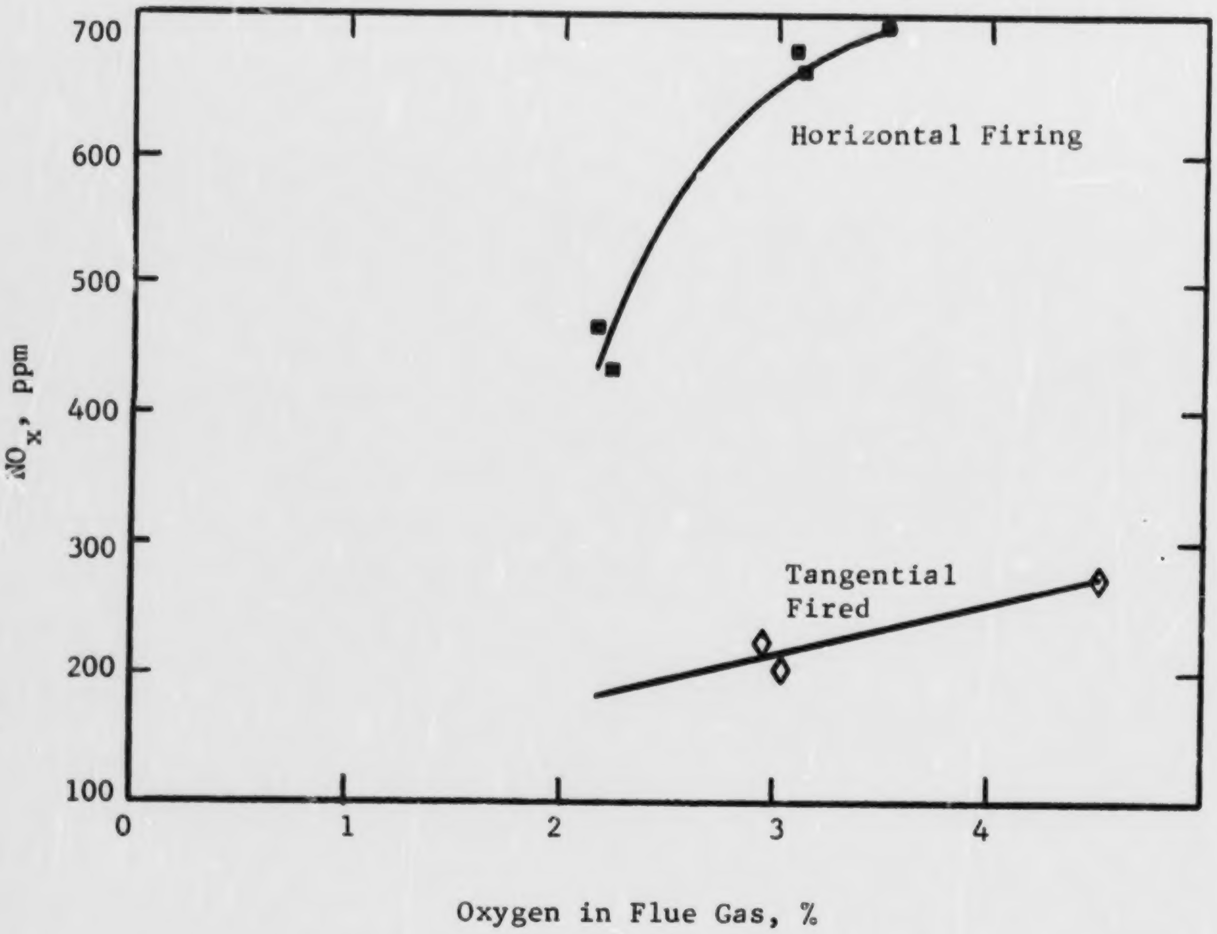
6.1. MODIFICATION OF OPERATING CONDITIONS

6.1.1 Low Excess Air Combustion

Low excess air combustion is a technique originally developed in the United Kingdom to overcome undesirable operating conditions such as low temperature corrosion and air heater plugging in oil fired boilers (476). Later, European boiler operators made further refinements in this type of operation claiming additional operating advantages, particularly improvements in furnace slagging and heating surface fouling (476). In the early 1960's this operating technique was introduced to public utilities in the United States and subsequently adopted as a regular practice at some oil fired power stations. While theory predicts a reduction of NO_x emissions with lower excess air, actual data are still limited on this type of operation. Investigations by Sensenbaugh and Jonakin (641) on oil fired boilers, reported in 1960, showed that NO_x emissions decrease as the oxygen content of the flue gas is reduced even at the higher levels of excess air. As shown in Figure 11, based on Figure 5 of reference (641),

Figure 11

Effect of Excess Air on NO_x Emissions From Oil Fired Boilers*

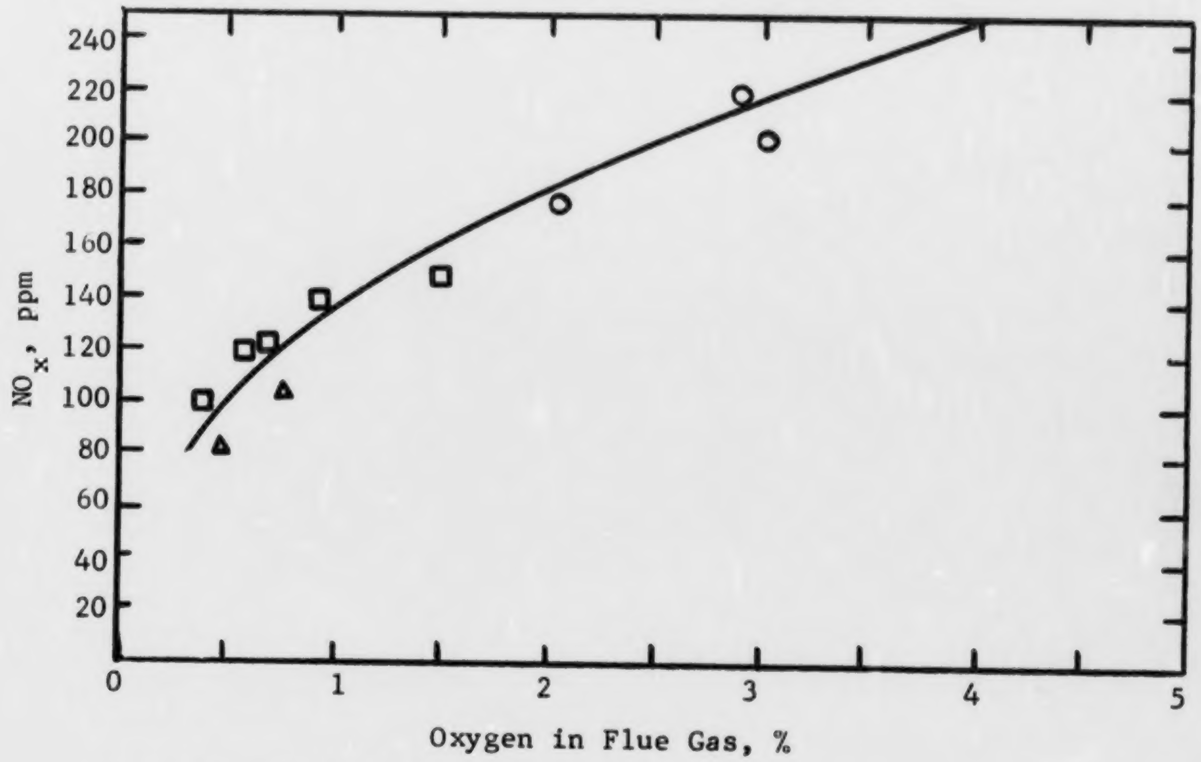


* After Ref. (641).

NO_x reductions of 36% in a horizontal oil fired boiler and 28% in a tangentially fired unit were obtained as flue gas oxygen content was decreased from 3.5-4.0% to about 2%. Subsequent investigations (422,405,476) at much lower excess air (2-3% excess air, 0.4-0.6% O_2) in oil fired installations indicate NO_x reductions of up to 63% can be achieved by lowering excess air from 15% to the 2-3% level. Figure 12 based on Figure 17 of the Fernandes, Sensenbaugh and Peterson report (422) illustrates the

Figure 12

NO_x Emissions From Oil Fired Boilers At Low Excess Air*

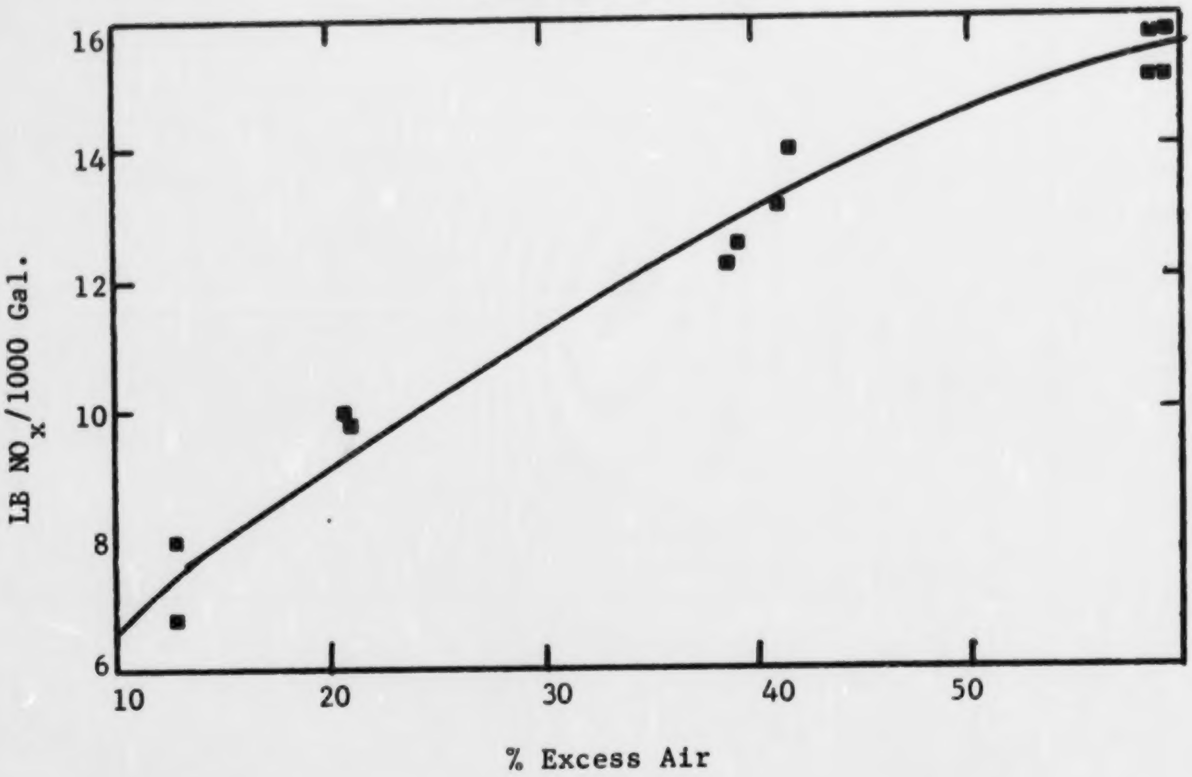


* After Ref. (422).

magnitude of NO_x reductions possible in oil fired boilers operating at low excess air. Similar effects have been observed in laboratory tests of an oil fired domestic heating installation (405) where the level of excess air is much higher than in the larger utility boilers. Figure 13 based on Figure 4 in reference (405) shows the effect of excess air on NO_x emissions in this type of equipment.

Figure 13

NO$_x$ Emissions From Heating Oil Combustion*

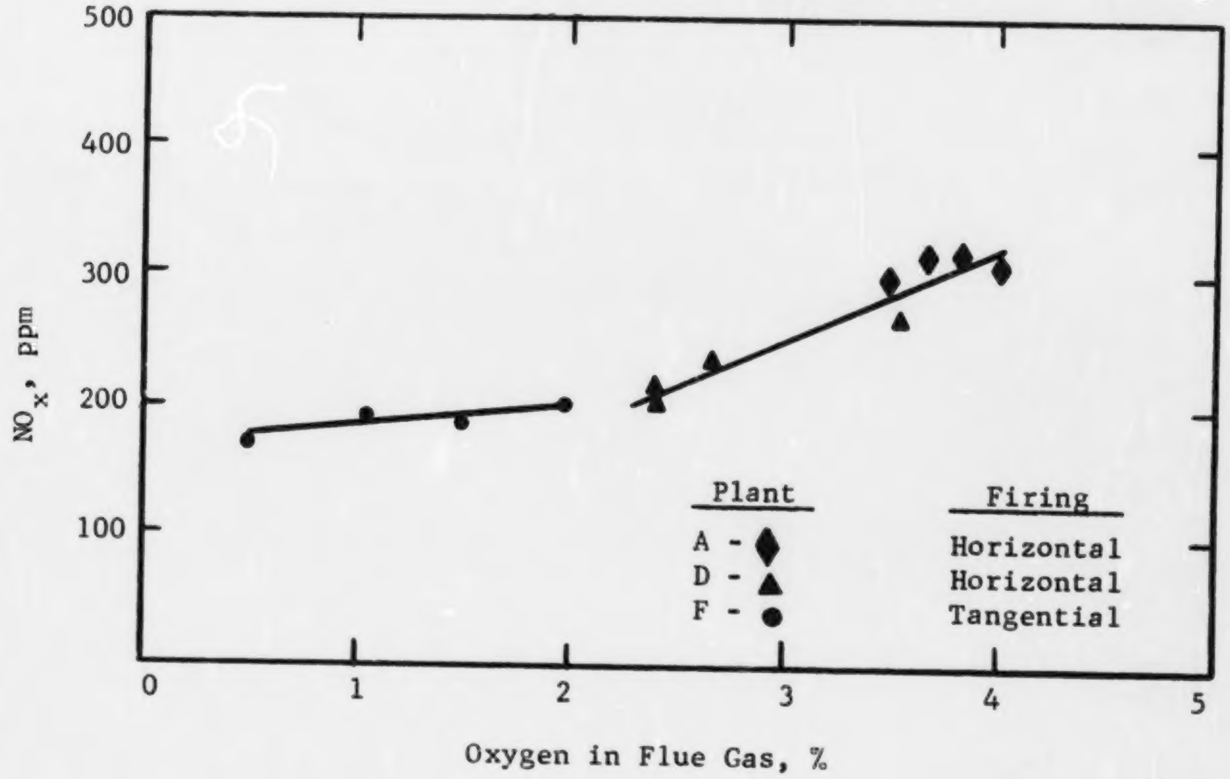


* After Ref. (405).

The effect of low excess air combustion in gas fired installations is not well documented. The only source of published data available, taken at relatively high excess air levels (422), provides an indication that similar decreases in NO$_x$ may be expected. Figure 14 based on

Figure 14

Effect of Excess Air on
NO_x Emissions From Gas Fired Boilers*



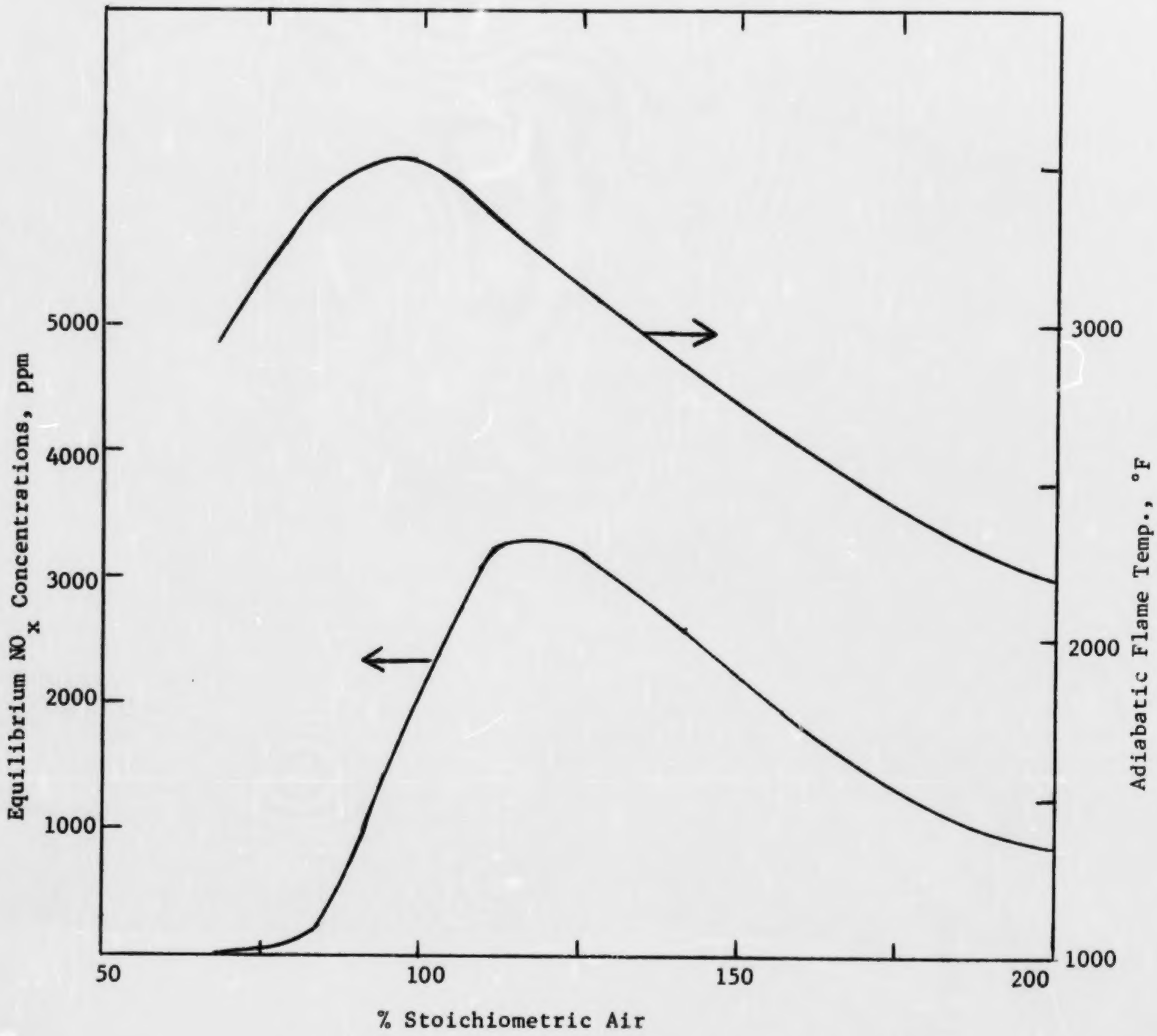
* After Ref. (422).

Figure 16, in reference (422), shows that this effect is more pronounced in a horizontally fired boiler than in one fired tangentially. Recently obtained unpublished data, however, demonstrate the favorable effect of low excess air combustion with gas. This information indicates that the effect is the same with either type of firing and that decreases in NO_x of up to 1/3 can be achieved using the low excess air technique.(*) It has been postulated that even though flame temperature increases with a decrease in excess air, tending to increase NO_x, the unavailability of atomic oxygen in the flame accounts for the observed decrease in NO_x. (405) Thermodynamic calculations shown in Figure 15 illustrate this point.

(*) Private communication.

Figure 15

NO_x Equilibrium in Methane-Air Flames



With proper care, low excess air firing practices can be applied to much of the existing combustion equipment in the United States to obtain lower NO_x emissions. The extent of the reductions possible, the cost of the modifications, and the applicability to given processes, however, are yet to be determined. For instance, it appears that low excess air operation may be difficult, if not impossible, to apply to pulverized coal installations. Imbalances between the coal, primary and secondary air streams in a pulverized coal system are extremely difficult to overcome.

It remains to be proven whether low excess air operation in a pulverized coal system is possible or practical and whether similar reductions in NO_x can be realized. Attempts to apply the low excess air combustion technique to pulverized coal firing have met with little success so far. As far as is known, there are no existing pulverized coal installations operating atlow excess air. Since the largest quantity of fuel consumed in the U.S. for electric generation is coal (most of which is pulverized coal), this control technique presents an important potential area for future research and development.

6.1.2 Flue Gas Recirculation

Flue gas recirculation is a technique which has been applied in specific combustion processes to achieve certain desirable operating conditions. Processes employing this technique provide some means for recycling a portion of the flue gases produced back to the combustion chamber using either forced or natural draft. The effect on combustion conditions depends on the point of injection into the combustion system, and the amount of gas recycled. Flue gas injected into the primary flame zone has the effect of (1) decreasing flame temperature and (2) diluting the combustion air and resultant flue gases. Where flue gas is introduced down-stream of the combustion process the effect is largely one of dilution. The quantity of gas recirculated is important and has a direct effect on the combustion modifications desired.

In the past 15 to 20 years, flue gas recirculation has frequently been used in large steam boilers as a means of controlling superheat temperature. A Babcock and Wilcox Company publication (Steam, 37th Edition, pages 13-15) states, "the recirculated gas is preferably introduced into the furnace at a location, and in a manner, so that the entering flue gas will reduce the effectiveness of the furnace heat absorption surface, decrease the residence of the hot gas stream in the furnace, and yet not interfere with the process of combustion." In the course of the California Joint Project in 1960-62 (475), the effect of flue gas recirculation on NO_x emissions was studied in a boiler using recirculation for steam temperature control. However, this type of recirculation did not involve the injection of flue gas into the active flame zone. Consequently, results were inconclusive and this type of recirculation was felt to be relatively ineffective. Unpublished information (*) recently obtained in a

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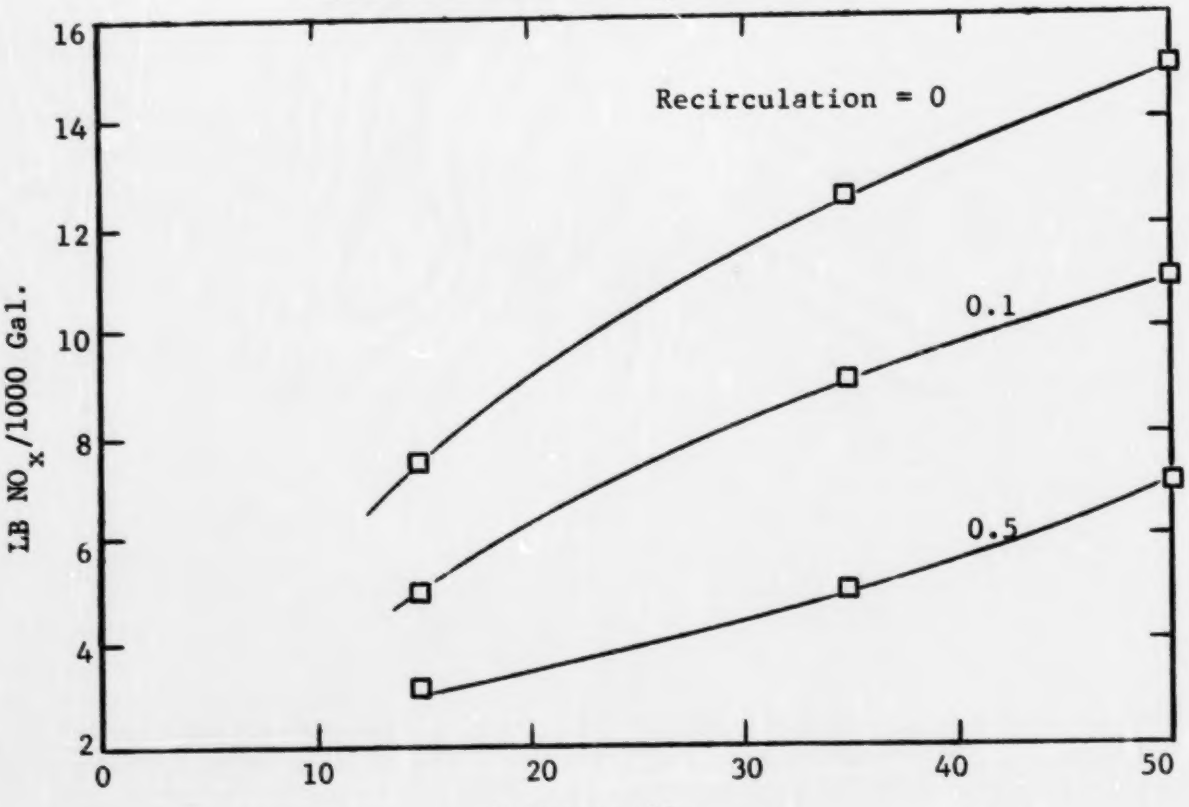
(*) Private communication.

similar test on a gas fired boiler, however, indicates a reduction of 20% in NO_x emissions with 20% flue gas recirculation. How much greater the reductions in NO_x might be with flue gases recirculated directly into the active flame zone is not known. Research in this area presents considerable challenge to determine the magnitude of NO_x reduction possible and to develop a method of recirculation for NO_x control compatible with the objectives of recirculation for steam temperature control.

Exhaust gas recycling has also been found to be effective in controlling NO_x in automotive exhaust. Investigators have shown (429)(442) that 80 to 85% reduction in NO_x can be achieved in the internal combustion engine, albeit at the expense of operability. Similarly, Esso studies of recirculation in laboratory tests of an oil fired domestic heating furnace (405) have shown potential reductions of 60% when recycling 50% of the flue gas, as shown in Figure 16 (405). The data presented in

Figure 16

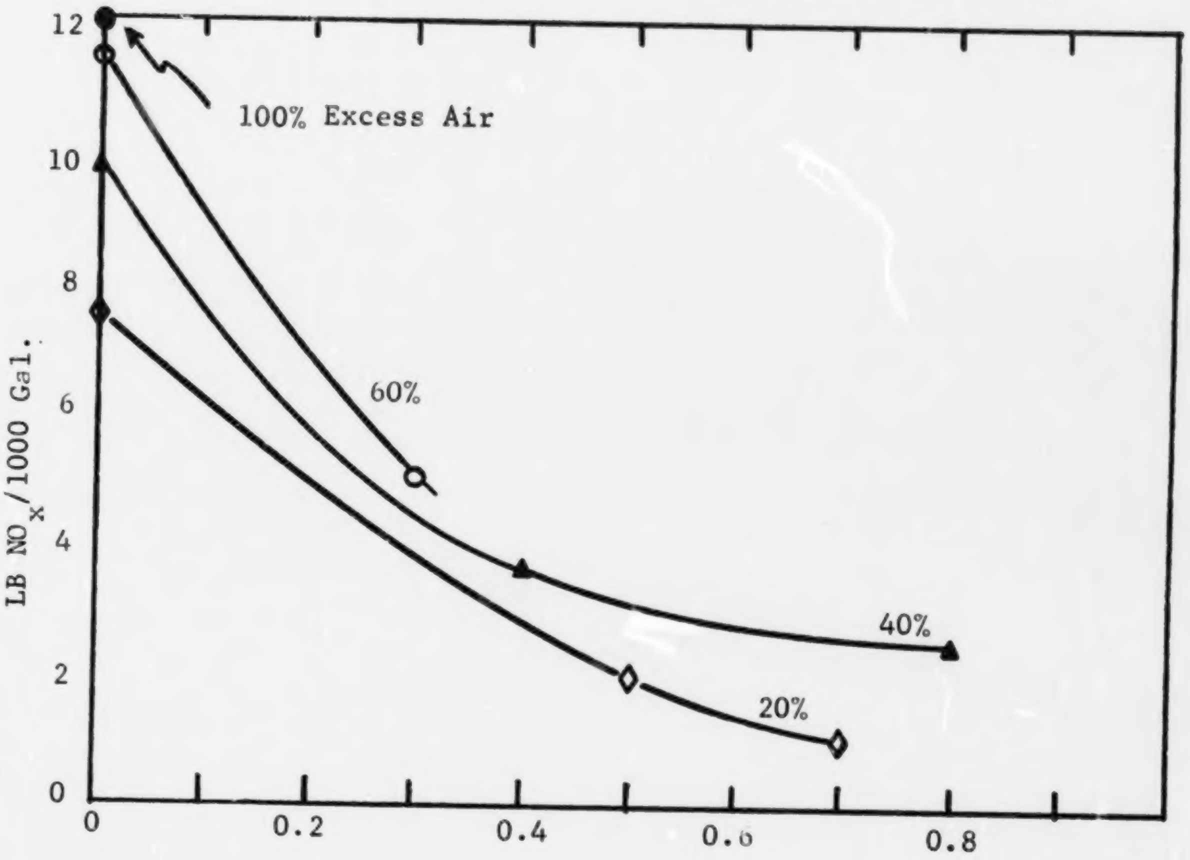
Combined Effect of Recirculation and Excess Air on NO_x Emissions*



* After Ref. (405).

Figure 17

Effect of Recirculation on NO_x Emissions From Heating Oil Combustion*



* After Ref. (405).

Figures 16 and 17 indicate that reductions in emissions up to 80% can be achieved by the combination of reducing excess air from 50 to 20% and recirculating 50% by volume of the flue gas. In addition to the reduction in NO_x, a further advantage of combining low excess air combustion with flue gas recirculation is that smokeless combustion could be achieved. Gas recirculation has also been employed in low temperature heating furnaces in industrial applications to achieve greater and more uniform heat transfer into the product. Vertical shaft lime kilns often employ recirculation to control calcining temperatures more effectively. The effect on NO_x emissions in the later cases, however, is not known but further investigation is warranted.

The mechanism for the reduction of NO_x emissions via flue gas recirculation has been attributed to the effect of decreasing flame temperature and to dilution of the available oxygen in the flame zone (405).

For gas fired appliances, it has been concluded by investigators at the Bureau of Mines that this reduction in NO_x is due only to the lowering of the flame temperature and not to reactant dilution (557). If true, the possibility of accomplishing the same end by other thermal means suggests the possibility of other solutions to the NO_x problem. Gas recirculation, regardless of its action in reducing NO_x, offers considerable potential for application to many existing installations, with the possible exception of those dependent on high flame temperature, i.e., melting furnaces. The extent of applicability of this type of combustion modification must still be investigated. The quantity of recirculated gas necessary to achieve the desired effect in different installations is important and can influence the feasibility of the applications. For instance, recirculating large quantities of gas in utility boilers can raise physical limitation problems in handling large quantities of gas, in addition to increased investment and operating costs.

6.1.3 Steam and Water Injection

Flame temperature, as discussed above, is one of the important parameters affecting the production of NO_x. There are a number of possibilities available to decrease flame temperature via thermal means. For instance, steam or water injection in quantities sufficient to lower flame temperature to the required extent may offer a simple control solution. Water injection may be preferred in many cases, due not only to its availability and lower cost, but also to its potentially greater thermal effect. In gas or coal fired boilers equipped for standby oil firing with steam atomization, the atomizer offers a simple means for injection. Other installations will require special rigging and an investigation program will be necessary to determine the degree of atomization and mixing with the flame required, the optimum point of injection, and the quantities of water or steam necessary to achieve the desired effect. The use of these techniques for NO_x control may carry with them some undesirable operating conditions, such as decreased efficiency, higher corrosion rates, etc., and these must also be evaluated.

Water injection was found to be very effective in suppressing NO_x emissions from an automotive engine.(481) NO_x emissions were decreased 90% by injecting water in a 1 to 1 ratio with the fuel. Engine power increased and a slight increase in specific fuel consumption was obtained. Substantial reductions in NO_x were also obtained with moderate rates of injection lending considerable support to this technique as a method of control. Steam injection in a large power boiler was also found to be effective, but specific data are not available at present.*

(*) Private communication.

6.1.4 Combustion with Oxygen

Economies have been achieved in the steel industry in certain processes by substituting oxygen for air. The cost of oxygen has decreased to a point where its use in some combustion processes may become feasible. This approach must be investigated in detail, as the higher flame temperatures with oxygen could offset the beneficial effect of lower nitrogen concentrations on NO_x emissions. Furthermore, with oil or coal-fired boilers the fuel nitrogen coupled with these higher temperatures may still result in significant NO_x emissions.

6.2. DESIGN MODIFICATIONS

6.2.1 Burner Configuration

The specific design and configuration of a burner has an important bearing on the amount of NO_x formed. Certain design types have been found to give greater emissions than others. For example, it appears that the spud type gas burner gives a higher emission rate than the radial spud type which, in turn, produces more NO_x than the ring type.(*) Similarly, the spray angle in oil atomizers can affect NO_x; narrower spray angles producing poorer atomization, have been reported to provide lower NO_x emissions (475) as opposed to the results of Barnhart and Diehl (407).

Some burners, such as the cyclone and vortex types, operate under highly turbulent, high intensity conditions. In field tests of conventional utility burners (475), adjustments made on burners to decrease turbulence to a minimum, reduced NO_x emissions by 40%, but resulted in unsatisfactory flame conditions. Throttling the burner registers to increase windbox pressure and turbulence increased NO_x emissions by more than 15%. It appears in general that long "lazy" flames in contrast with the short, intense flames usually considered desirable for combustion seem to favor lower NO_x emissions.

In the course of the California investigations in the late 1950's,a two-stage combustion type of burner was developed and is currently being used in a number of Los Angeles County power stations. In this type of burner about 95% of the stoichiometric air needed for combustion is admitted to the flame through the burner throat. The remainder of the air required for complete combustion is injected through ports above the burner to complete the burnout of the initial combustion phase. Operating under such conditions reductions of 30% in NO_x emissions were observed (407), while admission of only 90% of the stoichiometric air into the primary zone resulted in a 47% reduction of NO_x.(407) This technique has been applied successfully to oil and gas firing, but to our knowledge, no data are available on coal-fired boilers.

(*) Private communication, L.A. Department of Water and Power.

The effect of two-stage combustion on NO_x emissions may be explained by a combination of several factors. First, there is a lack of available oxygen for NO_x formation in the first stage operated under substoichiometric air conditions. Second, the flame temperature is lower in this first stage than in normal combustion. Third, to the degree that heat is removed between stages, the maximum flame temperature in the second stage is lower than for single stage combustion. Fourth, the effective residence time available for NO_x formation at the peak temperatures reached in the second stage may be reduced.

Based on the effects observed with the use of two-stage combustion, it is worthwhile to consider the extension of this technique to multi-stage combustion for improved NO_x emission control. As a more remote possibility, the staged injection of the fuel instead of air may result in a time-temperature-concentration profile favoring low NO_x emissions.

6.2.2 Burner Location and Spacing

Although data are scarce regarding the effect of burner spacing and location on NO_x, potentially these are important variables. The interaction between closely spaced burners, especially in the center of a multiple burner installation, could be expected to increase flame temperature at these locations. The tighter the spacing and the decreased ability to radiate to cooling surfaces, the greater the tendency toward increased NO_x emissions. This effect is illustrated by the higher NO_x emissions from larger boilers with greater multiples of burners and tighter spacing, as discussed in Section 6.4.

Tangential firing has been demonstrated as a useful design, representing a change from other types of burner location and spacing. Burners in a tangentially fired boiler are located in the corners, firing on a tangent to a circle at the center of the furnace. As a result, individual burner flames have very little opportunity to interact with one another and the flames radiate widely to the surrounding cooling surfaces. Tangential firing can produce reductions in NO_x of up to 50% compared with front or opposed fired furnaces.(422) This significant effect should be evaluated further for potential NO_x control in other types of combustion processes.

6.2.3 Fluidized Bed Combustion

Combustion of fossil fuels in fluidized beds may prove to be useful for NO_x control. Based on the excellent heat transfer characteristics of fludized bed combustion processes, the average bed temperature is very low (1600-1800°F) compared with conventional flame temperatures. Because of the low bed temperatures, only small amounts of NO_x should be formed based on the thermodynamic equilibrium under these conditions.

In spite of this favorable outlook, experimental data reported at the First International Conference on Fluidized Bed Combustion (Heuston Woods, Ohio, November 1968) did not show the expected reduction in NO_x emissions. For example, Pope, Evans and Robbins measured about 0.3 lb. $NO_x/10^6$ BTU fired in their coal burning pilot unit, which is the same as the emissions measured from stoker-fired units of similar capacity.

The reasons for the high levels of NO_x emitted from fluidized bed combustions are not yet known. Possibly, high local surface temperatures in the bed, or the oxidation of the nitrogen in the fuel, or both of these factors may contribute to the observed high levels of NO_x. Continuing developments with this technique may eventually result in substantial reductions of NO_x.

6.2.4 Small Combustion Equipment

The largest number of combustion devices in existence are installed in single family residences. Most of this equipment is gas fired. These small sources of NO_x, such as hot water heaters, residential space heating furnaces, etc. are difficult to modify economically.

Premixed flames have been shown to produce lower quantities of NO_x than diffusion flames in laboratory experiments.(620)(621) The application of this type of burner, eliminating or limiting the use of secondary air, may have an undeveloped potential for the economic modification of existing and new gas-fired equipment. Thus, substantial reductions in NO_x emissions from a wide segment of small pollution sources may be possible.

6.3. HEAT RELEASE RATE

The heat release in a given furnace volume has an important bearing on the flame temperature produced. The amount of cooling surface surrounding the combustion zone not only has an effect on the flame temperature but also affects the quench rate in the flame. The interaction between these two factors influences the NO_x emission rate. The trend in the public utility industry is toward much larger boiler/turbine installations than those presently in existence. Firing rates in these units, of necessity, has increased with resultant higher flame temperatures. The installation of a larger number of burners (Multiples) in these units is required to achieve the desired firing rate. The result is that the burners and the flame are spread throughout a wider portion of the furnace.

In the larger units, a greater portion of the furnace volume is filled with flame and the relative amount of cooling surface directly exposed to the flame is decreased. The apparent result is an increase in NO_x emissions. The factors influencing this phenomenon are not yet fully understood. Furthermore, some investigators have found NO_x emissions varying from 200 to 1200 ppm in different boilers having the same heat release rates. In evaluating heat release rates on NO_x emissions, other potential factors must obviously be considered.

Clearly, heat release rate and heat removal are coupled factors in affecting flame temperatures and hence NO_x emission rates. This will require a detailed understanding of the operating characteristics of furnaces and other combustion equipment, to derive the maximum benefit for NO_x control at the cost of relatively simple modifications.

6.4. EFFECTS OF FUEL TYPE AND COMPOSITION

Fuel type and composition has an important effect on resultant NO_x emissions. As shown in Table 3, Section 4, emissions from coal firing are highest in the three major use categories. Conflicting data are available on the relative position of emissions from oil and gas firing. According to the data in Table 3, oil is next highest in the Electric Generation & Industry sectors but lower than gas in Household & Commercial uses. Gas is lowest except for the Household & Commercial sector but only slightly higher than oil. More recently acquired data, however, as shown in Table 4 indicate that gas emissions are higher than for oil in many large installations by about 20% on the average. This differs markedly from Table 3 and the data developed in the Los Angeles County Joint Project of 1960-62 (475). The earlier study indicated gas emissions on the average 50% lower than for oil firing. The causes for these differences have not been assessed yet. However, for large boilers it has been suggested that the higher emissivity of oil flames provides a more rapid radiative heat removal rate than non-luminous gas flames, hence resulting in a lower effective residence time at peak temperatures.*

Interestingly, the use of two paraffinic low sulfur fuel oils in Los Angeles power stations has produced roughly 40% lower NO_x emissions than the normal California type fuel oil containing about 1.7% sulfur. The data in Table 4 indicate these trends. These data confirm that fuel composition, at least for fuel oil, can be important. Table 26 compares the other fuel property differences of the California cracked residual fuel oil with the low sulfur content Indonesian fuel. Aside from the differences in sulfur, these fuels show important differences in carbon to hydrogen ratios, ash, metals, gravity, and viscosity. Of particular interest is the large differences in nitrogen content, on the order of about 4/1. This could be a very important factor. All of the quality differences noted, either combined or separately, may contribute to the differences in NO_x emission rates. No proof as yet has been advanced to account for the lower NO_x rate, but it appears highly unlikely that the difference in sulfur content is important. Research work aimed at determining the influence of the important differences in the composition of a given fuel appears to be warranted.

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* "Analysis of Air Pollution Problems at Moss Landing" Stanford Research Institute.

TABLE 26

Ultimate Analysis (%)	California Cracked Residual Fuel Oil	Low Sulfur Oil
Carbon	86.29	86.44
Hydrogen	9.9	12.72
Nitrogen	1.0	0.24
Sulfur	1.7	0.25
Ash	0.06	0.013
Oxygen (by difference)	0.05	0.337
Ash Analysis (PPM)		
Vanadium	95	1
Nickel	110	7
Iron	75	2
Copper	1	.2
Silicon	10	3
Sodium	25	Trace
Calcium	15	3
Magnesium	5	1
Other Physical Properties		
Gravity	5	22-30
Flash Point	225	195-350
Viscosity, SSF @ 122°F	1500	-
Viscosity, SSU @ 210°F	-	50-250°F
Sediment & Water, Vol. %	1.0	0.05-0.30
Btu/bbl, Gross	6,450,000	5,860,000-6,260,000
Pour Point	-	105-115

6.5 MATHEMATICAL MODEL FOR NO_x FORMATION IN COMBUSTION PROCESSES

As discussed in the introductory part of Section 6 of this report, high temperature combustion of fossil fuels with air results in the fixation reaction between nitrogen and oxygen.

In order to guide the design of furnace-boilers emitting low amounts of NO_x, it is desirable to develop a mathematical model which could predict the rate of formation of NO_x as a function of combustor design and operating parameters. As an initial approach to this problem, the literature on fossil fuel combustion and NO reaction kinetics and thermodynamics is being reviewed.

Parallel with this review of the literature, an idealized mathematical model is being formulated aimed at predicting the effects of combustion parameters on NO_x formation. It is hoped that such a model could provide useful information for guiding research and development efforts on combustion modification techniques for minimizing NO_x emissions.

Combined with the detailed evaluation of the literature on combustion processes, the results obtained from this initial modeling effort should also be useful for the selection of more detailed, sophisticated mathematical models capable of guiding the design of low NO_x-emitting furnaces.

The initial model selected concerns itself with a homogeneous gas phase reaction system. To simulate the combustion of natural gas, methane combustion was selected as the heat generation input for the model.

The detailed chemistry of methane combustion is complex, as typical for gas phase free radical chain reaction processes. Under steady state conditions, the rate controlling steps appear to be the reactions of methane and carbon monoxide (an intermediate product) with hydroxyl free radicals (548).

$$CH_4 + OH \rightleftharpoons CH_3 + H_2O \qquad (27)$$

$$CO + OH \rightleftharpoons CO_2 + H \qquad (28)$$

Corresponding to these rate controlling steps, the "overall" kinetics of methane combustion can be described by a two-step sequence of reactions:

$$CH_4 + 3/2\ O_2 \rightleftharpoons CO + 2H_2O \qquad (29)$$

$$CO + 1/2\ O_2 \rightleftharpoons CO_2 \qquad (30)$$

Rate expressions for methane and CO combustion have been determined by Morgan in a jet-mixed reactor (595)

$$-\frac{d(CH_4)}{dt} = 4.7 \times 10^{15}\ e^{-56,000/RT} \left(f_{CH_4}\right)\left(f_{O_2}\right)^{1/2}\left(f_{H_2O}\right)^{1/2}\left(P/RT\right)^2$$

$$-\frac{d(CO)}{dt} = 1.8 \times 10^{10}\ e^{-25,000/RT} \left(f_{CO}\right)\left(f_{O_2}\right)^{1/2}\left(f_{H_2O}\right)^{1/2}\left(P/RT\right)^2$$

where combustion rates are in units of g. moles/liter/sec., and f represents the mole fraction of the reacting species. These rate expressions are being considered as the basis for the mathematical model being developed.

In addition to the heat generation term provided by the rate of combustion of methane, the other input functions for the mathematical model will include specified flow area, pressure and heat flux profiles. Alternately, heat transfer rates may be specified instead of heat flux profiles in the model to be developed.

The combustion zone itself will be represented in the model by a series combination of stirred reactor zones of arbitrarily adjustable volumes. The first volume element serves as the ignition zone for the air/fuel mixtures. By selecting a sufficiently large number of sufficiently small stirred reactor zones, this type of model converges into a combination of a stirred ignition zone followed by a plug flow reactor.

To formulate the kinetics of NO formation, the Zeldovich-type chain reaction kinetics (discussed earlier in Section 6) will be incorporated into the model. The output of this model development should consist of NO concentration-time profiles as affected by the variations of the combustion parameters.

Based on the results available from the initial NO_x model formulation, means will be sought to incorporate additional features that will permit evaluating the effects of some of the known combustion modification techniques. Thus, it may be possible to extend the initial NO_x formation model to include flux gas recirculation, staged combustion and the simulation of mixing effects.

7. FUTURE STUDIES

The first objective of the program planned for the continuation of this contract is to finalize the NO_x emission source inventory. The steam-electric plant questionnaire data to be collected by hand delivery to 19 selected utility companies will be analyzed and integrated with the NO_x emission inventory already developed for combustion sources. The questionnaire results will be tabulated according to plant size, type of fuel, and type of firing. NO_x emissions from electric power plants calculated for the period 1950-1967 will be revised using emission factor data developed for regional and total U.S. applications.

For other contributing sectors (domestic, commercial and industrial) the regional and nationwide NO_x inventory data will be developed to the extent warranted by their importance. This will form the basis for the total NO_x emission inventory for all sources covering the period 1950-1957.

Estimates of NO_x emissions to the year 2000 for the U.S. will be based on the analysis of forecasts of energy supply, technological innovations, industrial and social-economic trends. Ranges of NO_x emission forecasts will be calculated, based on the degree of applications of possible control methods for both stationary and mobile sources.

The identification of existing control technology for stationary sources of NO_x is close to completion at this point in the program. Studies will be continued to devise potential new NO_x control methods in the three broad categories of the control technology program: combustion modification, in-process NO_x removal, and other industrial process modifications. Work on potential combustion modification techniques will be supported by mathematical modeling studies of NO_x formation in combustion processes.

In the study of flue gas treatment technology, the desirability of simultaneous NO_x and SO_x removal will be a major consideration.

All technically attractive control methods will be assessed from the standpoint of cost-effectiveness. This assessment of NO_x control techniques, combined with specific research needs identified in this study will guide the formulation of the two five-year research and development program plans.

8. ATTACHMENTS

ATTACHMENT 1

STEAM-ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967

ESSO RESEARCH AND ENGINEERING COMPANY
U.S. DEPARTMENT OF HEW, NATIONAL AIR POLLUTION CONTROL ADMINISTRATION CONTRACT (NUMBER PH-22-68-55)
"SYSTEMS STUDY OF NITROGEN OXIDE CONTROL METHODS FOR STATIONARY SOURCES"

Firm Name ______________________ Mailing Address ______________________

Plant Name and Location ______________________ ______________________

____

Person to Contact Re This Report ______________ Title ______________ Phone No. ______________

SECTION I - BOILER INFORMATION.(1) Complete for each boiler or group of identical boilers (if necessary attach additional sheets).

1.	Boiler Number or Numbers					1.
2.	Steam Press, P.S.I.					2.
3.	Maximum Con't Rating (MCR), 1000 lb. stm./hr.					3.
4.	Initial Year of Operation					4.
5.	Manufacturer					5.
6.	Steam Temp., °F - Superheater/Reheater	/	/	/	/	6.
7.	Design - Suction or Pressurized Furnace	S P	S P	S P	S P	7.
8.	- Wet or Dry Bottom	W D	W D	W D	W D	8.
9.	- Furnace Volume, Cubic Feet					9.
10.	- Furnace Heating Surface, Sq. Ft.					10.
11.	Stack Number(2)					11.
12.	Stack Height/Diameter at Top, Feet	/	/	/	/	12.
13.	Type of Firing(3) V,T,FW,S,Cy,HO,Tu					13.
14.	Mixed Fuel(4), CF, SF					14.
15.	Oil: Steam or Mech Atomization(5)	St. Me.	St. Me.	St. Me.	St. Me.	15.
16.	Oil Pressure, PSI - Max.					16.
17.	Gas: Burner Design(5)					17.
18.	Coal: Burner Design(5)					18.
19.	Windbox Pressure Inches H_2O (Full Load)					19.
20.	Flyash Reinjection(6)					20.
	Steam Temperature Control:					
21.	- Attemperation(6)					21.
22.	- Flue Gas Recirc., % Max.- Before/After Burner	B A	B A	B A	B A	22.
23.	- Tilting Burners(6)					23.
24.	Two-Stage Combustion(6) (See Section II)					24.
25.	Boiler Efficiency-% (Full Load) Coal/Oil/Gas	/ /	/ /	/ /	/ /	25.

- - - - - - -

(1) Please attach boiler outline sketch similar to attachments.
(2) Give plant stack designation and height of stack into which boiler discharges.
(3) Vertical, Tangential, Front-Wall, Stoker, Cyclone, Horizontally Opposed, Turbo Furnace.
(4) Combination Firing (Alternate Burners on Different Fuels), Simultaneous Firing (2 Fuels in Same Burner/s).
(5) See attached sketches. Indicate burner configuration similar to Sketch A, B, C. If different, indicate type and manufacturer.
(6) (Yes or No).

FUEL DATA(7), Tons/Hr., bbl/hr., 1000 CF/hr.	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	
26. Max. Con't Rating (Full Load)													26.
27. 3/4 Load													27.
28. 1/2 Load													28.
29. Annual Consumption (1967) 1000 Tons, 1000 bbls., or 10^6 cu. ft.													29.
30. Av. Heat Content, BTU/lb., gal. or CF (Dry)													30.
31. Sulfur Content - Weight %(8)													31.
OPERATING DATA													
32. Flue Gas Rate - Full Load, 1000 lbs./hr.													32.
33. " " " - 3/4 Load " " "													33.
34. " " " - 1/2 Load " " "													34.
35. Excess Air/O_2,% - Full Load	/	/	/	/	/	/	/	/	/	/	/	/	35.
36. " " " - 3/4 Load	/	/	/	/	/	/	/	/	/	/	/	/	36.
37. " " " - 1/2 Load	/	/	/	/	/	/	/	/	/	/	/	/	37.
38. NO_x Emissions, ppm(9) (Calc. to 3% O_2) - Full Ld.													38.
39. " " " " " " " - 3/4 Ld.													39.
40. " " " " " " " - 1/2 Ld.													40.
41. No. of Burners - Full Load													41.
42. " " " - 3/4 Load													42.
43. " " " - 1/2 Load													43.
44. Preheated Air Temp. °F													44.
45. Burner Flame " "													45.
46. Flue Gas Entering Superheater " "													46.
47. Flue Gas Entering Economizer " "													47.
48. Flue Gas Entering Air Preheater " "													48.
49. Flue Gas Leaving Air Preheater " "													49.
50. Oil Atomizing Temperature °F													50.
51. Flue Gas Cleaning Equip.,(10) E,WS,Mech,Bag													51.
52. Efficiency of Gas Cleaning Equipment - %													52.

LOAD VARIATION (Number of Boiler Hours in Typical Week)	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	
53. No Load									53.
54. Less Than 40% Load									54.
55. 40-59% Load									55.
56. 60-79% Load									56.
57. 80-99% Load									57.
58. Full Load									58.

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(7) Assume single fuel firing.

(8) Please attach typical analysis of fuel (ultimate preferred), ash and flyash. Also include % of ash collected as flyash, % ash collected as bottom ash. If analysis data not readily available, please give name and address of supplier.

(9) Complete only if data are available from stack tests (also state method used for NO_x analysis).

(10) Electrostatic Precipitator, Wet Scrubber, Mechanical, Bag Filter.

SECTION II - TWO STAGE COMBUSTION INFORMATION SHEET

1. Boiler Number or Numbers				
2. Installed: A As Original Equipment or B Addition	A B	A B	A B	A B
3. Incremental Installation Cost, 1000$				
4. Reduction in Boiler Efficiency (If Any), %				
5. Increased Maintenance Cost (If Any), $ Per Year				
6. Incremental Operating Costs,* Mils Per 1000 lbs. of Steam				
7. Reduction in NO_x Emissions at Full Load, %				
8. Other Benefits:				
9. % Stoichiometric Air: A 1st Stage, B 2nd Stage Ports	A B	A B	A B	A B

- - - - - - - - -

* If Available.

Plant Name ______________________ Location ______________________

SECTION III - PEAK SHAVING UNITS (Gas Turbines - Internal Combustion Engines)

1. Unit Number(s) (Group Identical Units)					1.
2. Nameplate Rating, KW					2.
3. Year Installed					3.
4. Manufacturer					4.
5. Manufacturers Model No.					5.
6. If Diesel: A, B, C, D, E (1)					6.
7. If Gas Turbine: A) Aircraft Type, B) Industrial Type					7.
8. Fuel Consumption, BTU/KW @ Full Load					8.
9. Kind of Fuel (Nat. Gas, Kerosene, Diesel Fuel, Etc.)					9.
10. Fuel Oil Analysis: (2) - Gravity, °API					10.
- Viscosity, SSU/100°F (or other)					
- Hydrogen % (if Available)					
- Sulfur, Ash (Wt. %)	S ___ A ___	S ___ A ___	S ___ A ___	S ___ A ___	
- Vanadium, Sodium (PPM)	V ___ S ___	V ___ S ___	V ___ S ___	V ___ S ___	
11. Average Heat Content of Fuel, BTU/lb., Gal., or Cu. Ft.					11.
12. Annual Fuel Consumption - 1967, Bbls, 1000's Cubic Ft.					12.
13. Operating Hours Per Year					13.
14. Exhaust Gas Temp, °F					14.
15. Inlet Gas Temp., °F (3)					15.
16. Fuel Air Ratio, lb. Fuel/lb. Air (3)					16.
17. Pressure Ratio (Compression) (3)					17.
18. Nitrogen Oxide Emission at Full Load, lb./Hour (4)					18.
19. Height of Stack, Ft.					19.

- - - - - - - -

(1) A 2-Cycle, Air Scavenged; B 4-Cycle Turbocharged; C 2-Cycle Normally Aspirated (NA) Low Speed (about 300 RPM); D 4-Cycle (NA) Medium Speed (about 1800 RPM); E 4-Cycle (NA) High Speed (about 3200 RPM).

(2) If not available, give name and address of fuel supplier.

(3) Applies primarily to gas turbine - available from manufacturer's catalog, etc.

(4) Fill in if measured by actual test and designate test method used.

ATTACHMENT 2

STEAM-ELECTRIC PLANT SURVEY
INSTRUCTIONS

SECTION I - BOILER INFORMATION

Although most of this questionnaire is self-explanatory, the following instructions are given to clarify and simplify specific lines. This form provides 4 columns for information on boilers. Information on boilers which are physically identical may be grouped into a single column. However, boilers of different size, type of firing, etc., should be listed in separate columns. (Please note example survey form.) Where an item is not applicable in a specific instance, insert N.A. rather than leaving the item blank.

Line 1 - Boiler Number or Numbers - Give the number of physically identical boilers.

Line 3 - Maximum Continuous Rating - Give either manufacturer's rating or sustained operating capability. However, it is important that Fuel Data on lines 26 through 29 are consistent with line 3 data.

Lines 9 and 10 - Furnace Volume and Heating Surface - From manufacturer's performance sheet.

Line 14 - Mixed Fuels - If two fuels are burned simultaneously in a single burner indicate SF, Simultaneous Firing (two fuels in same burner). Indicate CF, Combination Firing, for two fuels burned simultaneously in separate burners.

Lines 15, 17 and 18 - See attached sketches. Indicate burner configuration similar to Sketch A, B, C. If different, indicate type and manufacturer.

Line 24 - If answer is yes, please complete Section II Two Stage Combustion Information Sheet.

Lines 26-8 - Fuel Data - Give fuel consumption assuming only one fuel burned at a time (no mixed or simultaneous firing).

Line 32 - Flue Gas Rate - CF/M from manufacturer's performance sheet.

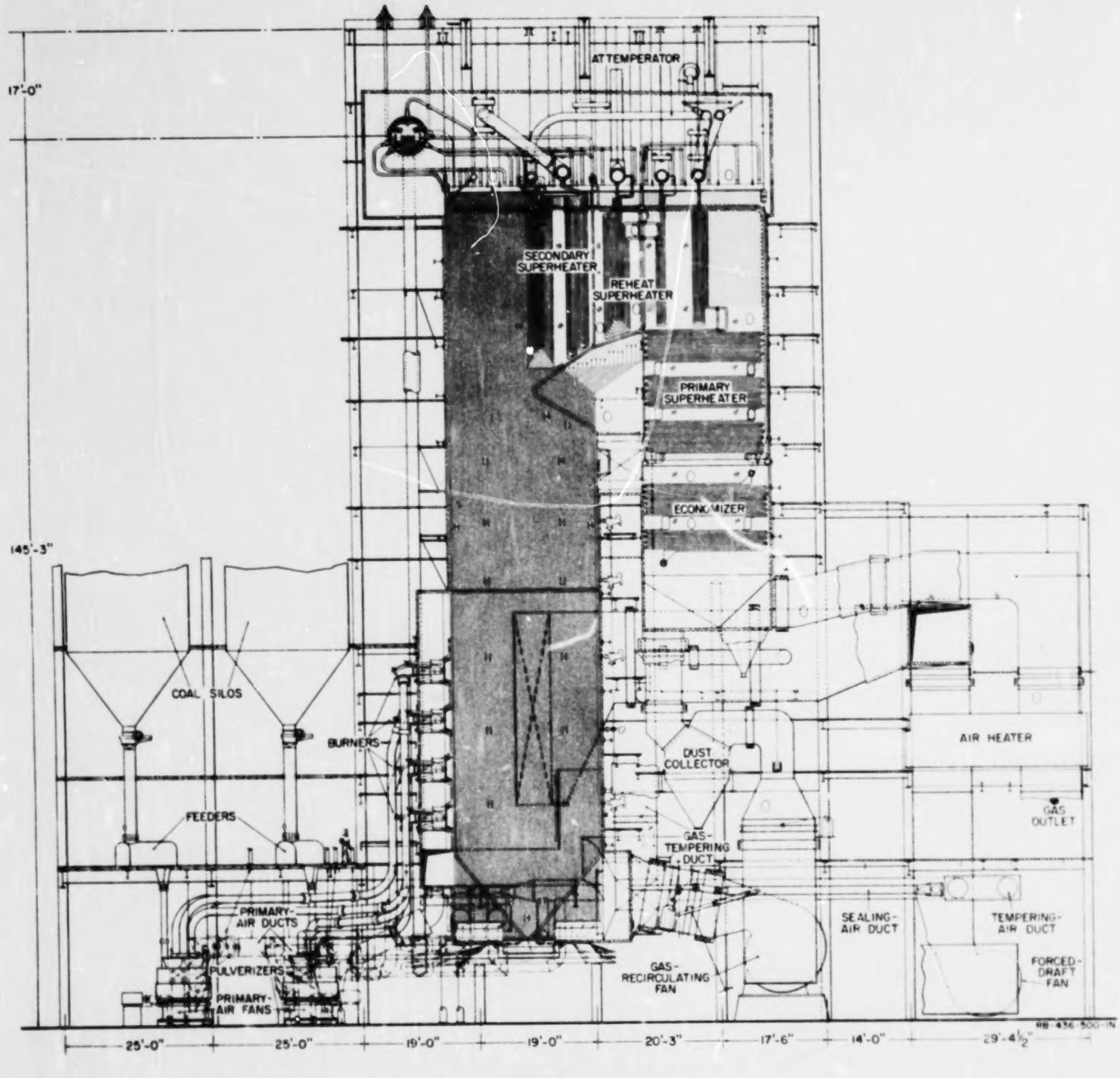
Lines 35-37 - Please give % excess air or O_2 in flue gas, depending upon whichever is available.

Line 45 - Complete only if data are available from measurements.

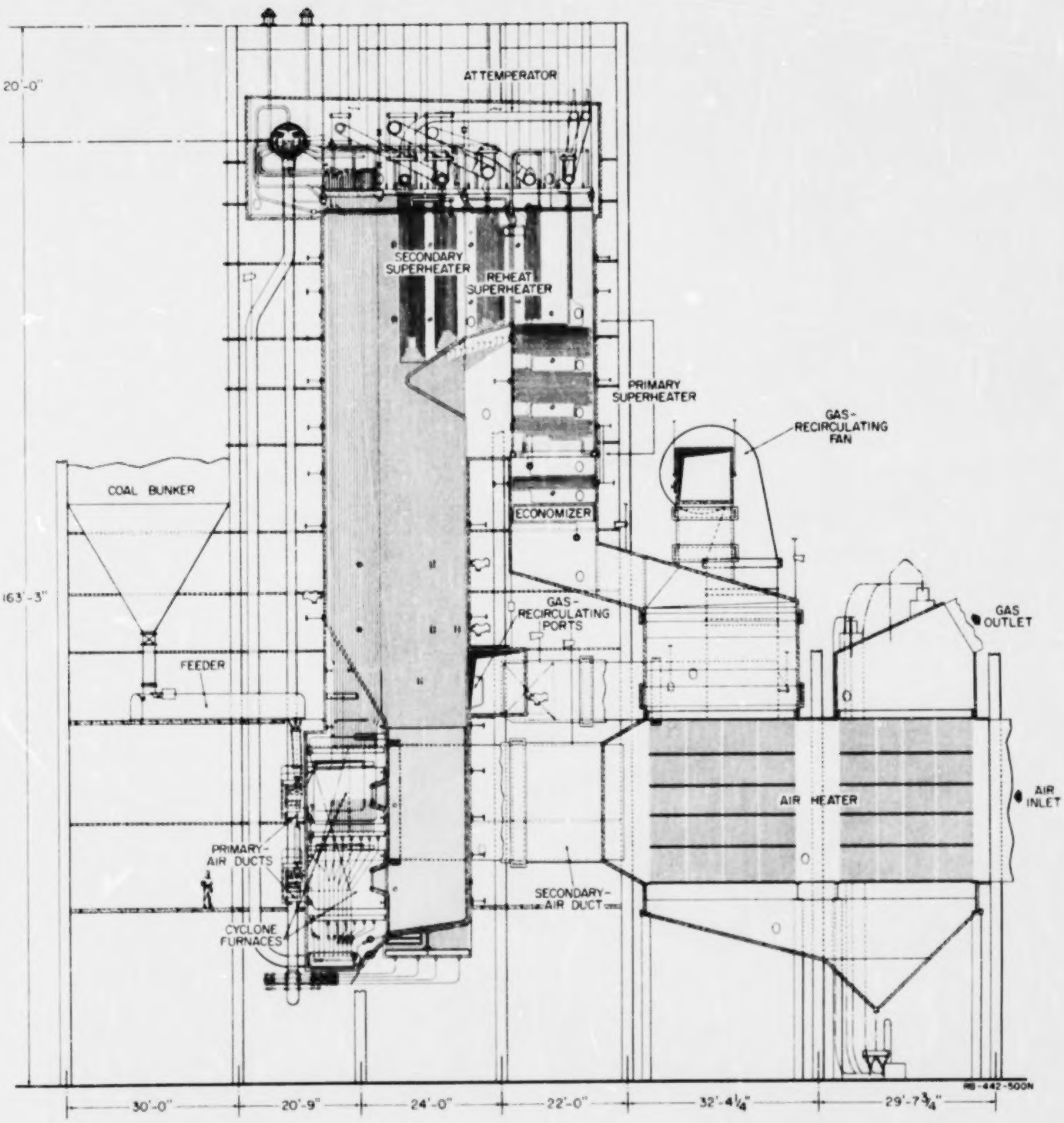
Line 46 - Generally available from manufacturer's performance sheet.

Lines 49-54 - Load Variation - Please estimate number of boiler-hours in typical week of summer and winter within each specified load range. Where a single column represents data from a number of identical boilers, report combined boiler-hours in each load range. See example survey form where the first column covers the identical boilers.

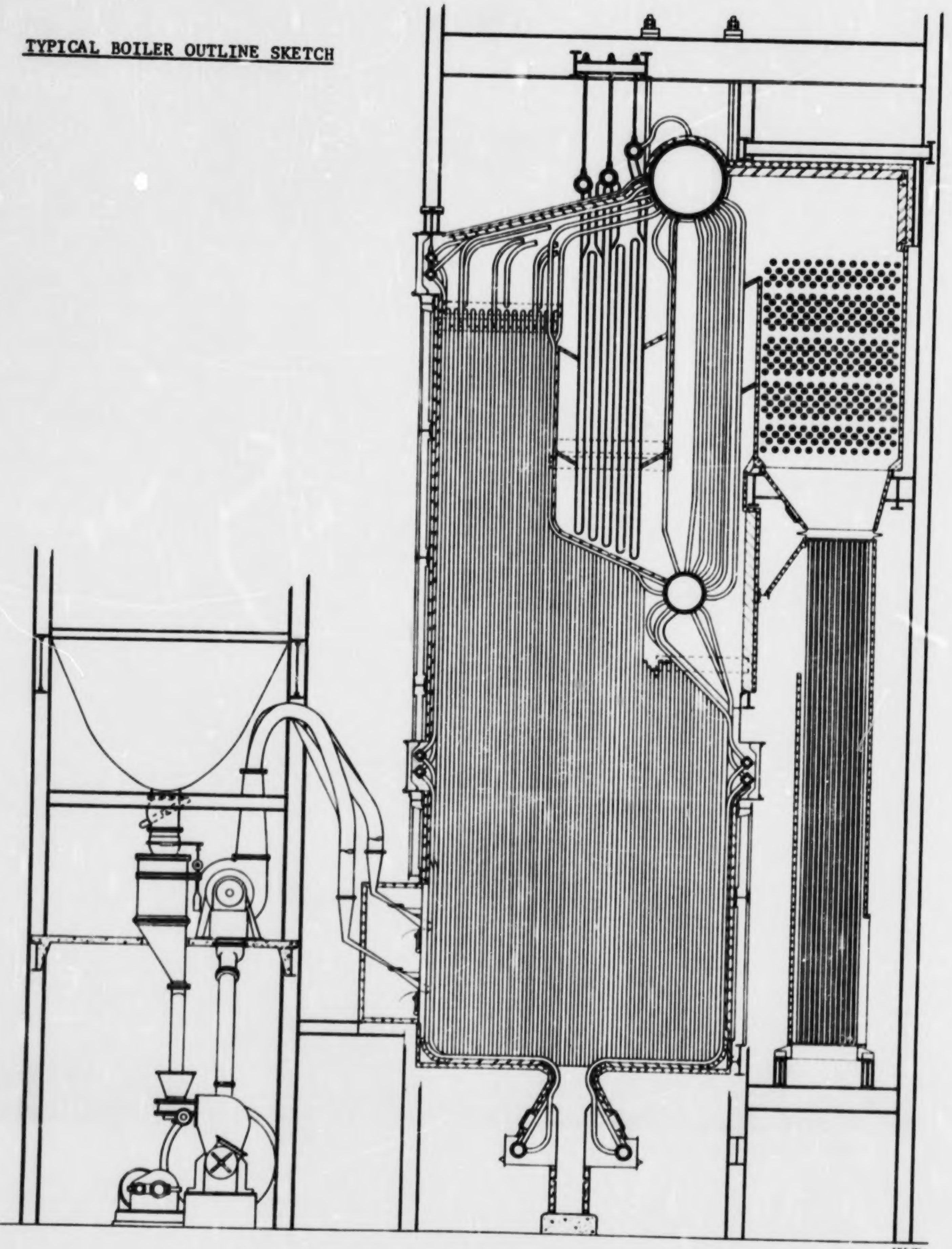
TYPICAL BOILER OUTLINE SKETCH


ATTEMPERATOR
17'-0"
SECONDARY SUPERHEATER
REHEAT SUPERHEATER
PRIMARY SUPERHEATER
ECONOMIZER
145'-3"
COAL SILOS
BURNERS
AIR HEATER
DUST COLLECTOR
GAS OUTLET
FEEDERS
GAS-TEMPERING DUCT
PRIMARY-AIR DUCTS
SEALING-AIR DUCT
TEMPERING-AIR DUCT
PULVERIZERS
GAS-RECIRCULATING FAN
FORCED-DRAFT FAN
PRIMARY-AIR FANS
RB-436-500-IN
25'-0"
25'-0"
19'-0"
19'-0"
20'-3"
17'-6"
14'-0"
29'-4½"

TYPICAL BOILER OUTLINE SKETCH


20'-0"
ATTEMPERATOR
SECONDARY SUPERHEATER
REHEAT SUPERHEATER
PRIMARY SUPERHEATER
GAS-RECIRCULATING FAN
COAL BUNKER
ECONOMIZER
163'-3"
GAS-RECIRCULATING PORTS
GAS OUTLET
FEEDER
AIR HEATER
AIR INLET
PRIMARY-AIR DUCTS
SECONDARY-AIR DUCT
CYCLONE FURNACES
RB-442-500N
30'-0"
20'-9"
24'-0"
22'-0"
32'-4¼"
29'-7¾"

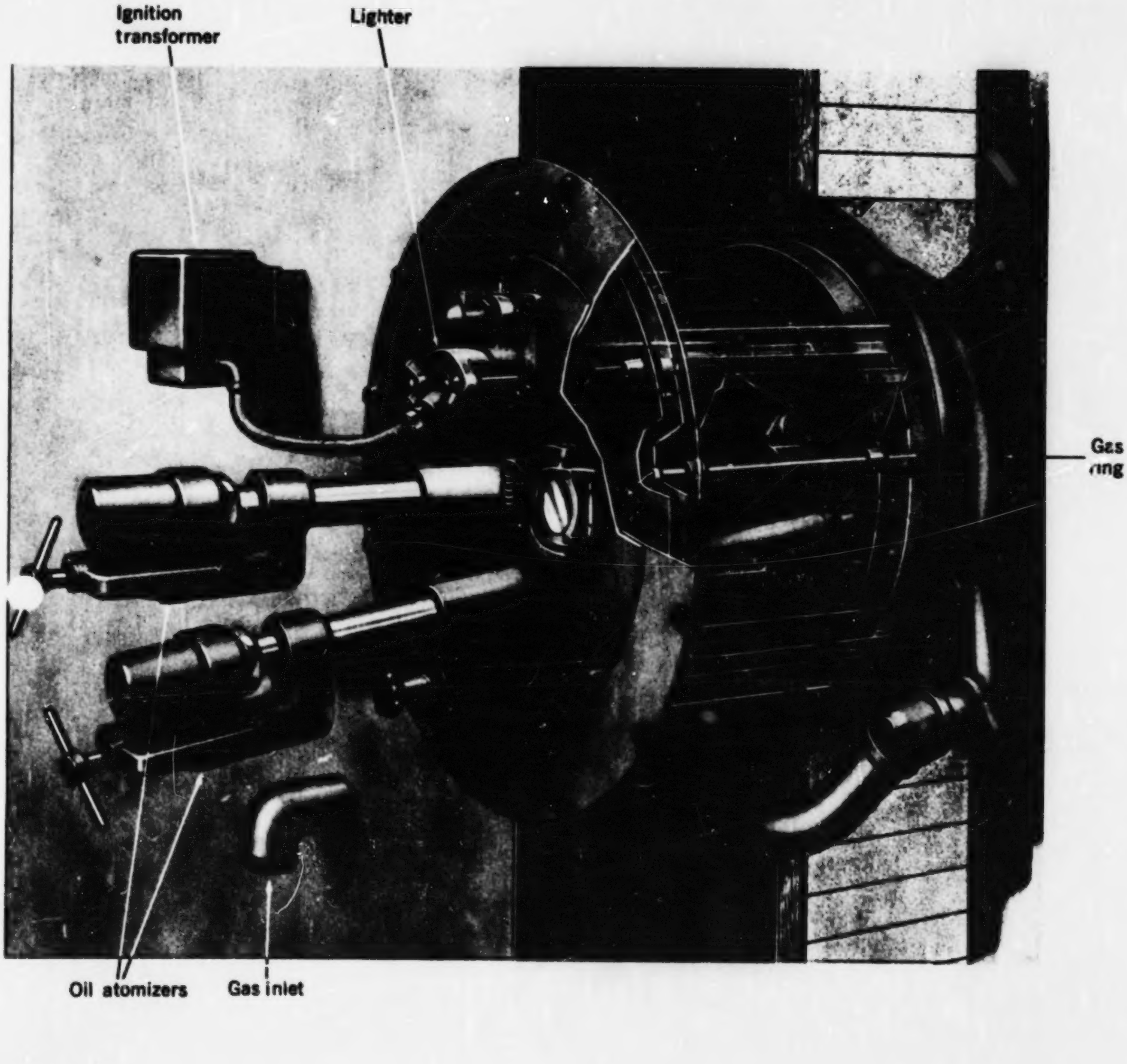
TYPICAL BOILER OUTLINE SKETCH



SKETCH A

GAS - RING TYPE BURNER

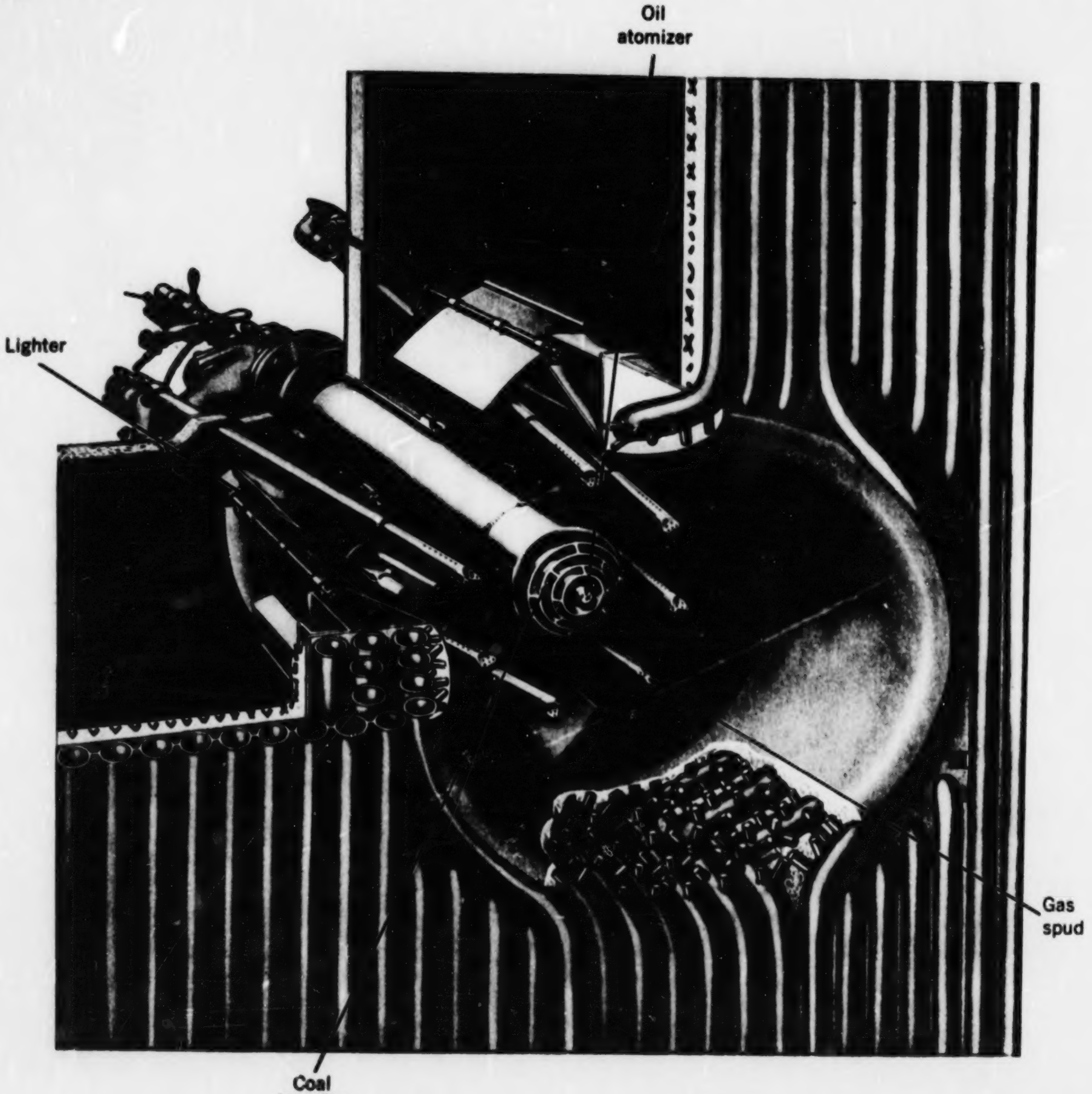
BDS
410
9242
12-66


Ignition transformer
Lighter
Gas ring
Oil atomizers
Gas inlet

SKETCH B

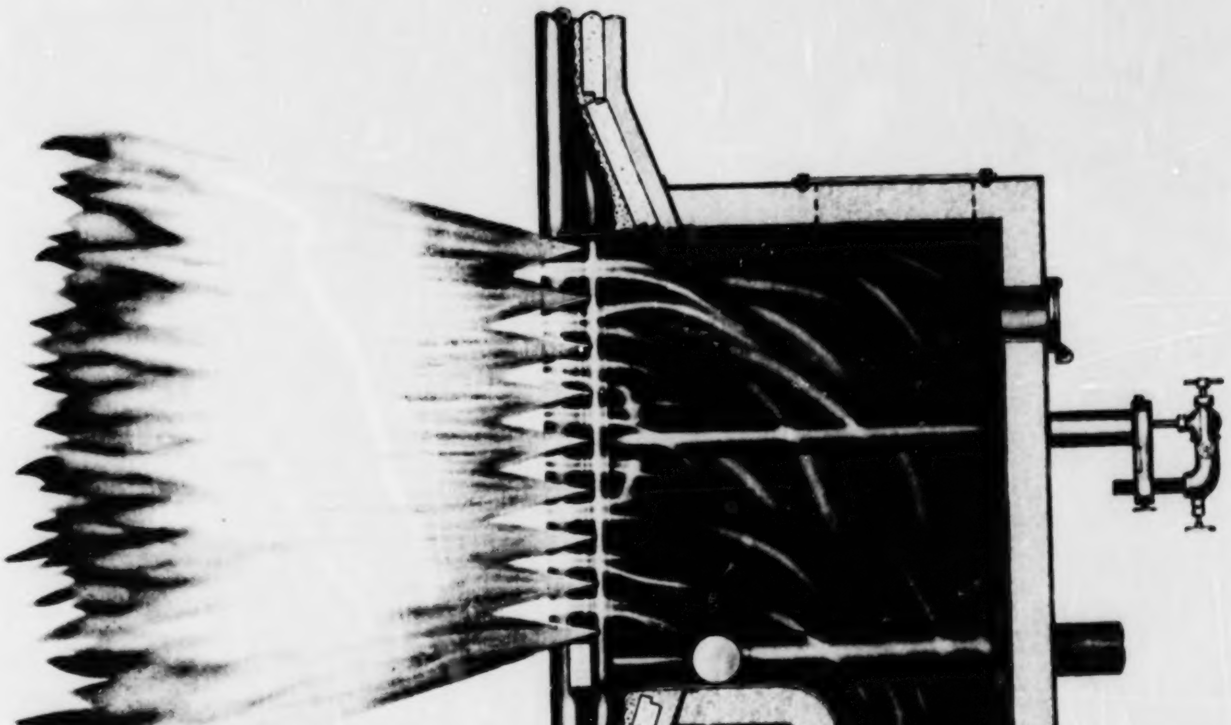
GAS - SPUD TYPE
OIL - CIRCULAR REGISTER
COAL - CIRCULAR REGISTER

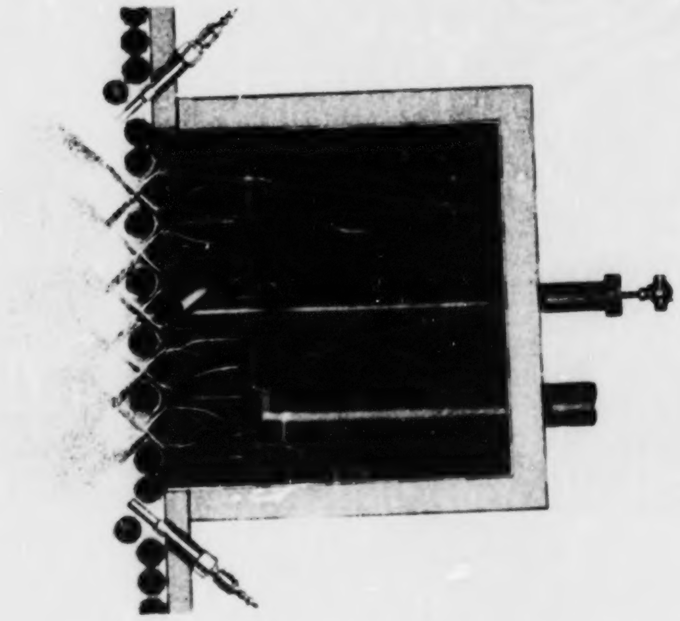
BDG
410
304LR2
10-65


Oil atomizer
Lighter
Gas spud
Coal impeller

SKETCH C

INTERTUBE TYPE - SHOWN FOR GAS AND OIL, SIMILAR FOR PULVERIZED COAL





ATTACHMENT 3

STEAM-ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967

ESSO RESEARCH AND ENGINEERING COMPANY
U.S. DEPARTMENT OF HEW, NATIONAL AIR POLLUTION CONTROL ADMINISTRATION CONTRACT (NUMBER PH-22-68-55)
"SYSTEMS STUDY OF NITROGEN OXIDE CONTROL METHODS FOR STATIONARY SOURCES"

Firm Name XYZ Electric Company

Plant Name and Location New York
New York

Mailing Address 1284 Rahway Avenue
Westfield, New Jersey 07090

Person to Contact Re This Report John Doe

Title Chief Mech. Eng.

Phone No. 201-474-3128

SECTION I - BOILER INFORMATION.(1) Complete for each boiler or group of identical boilers (if necessary attach additional sheets).

1.	Boiler Number or Numbers	3 Boilers	1			1.
2.	Steam Press, P.S.I.	2400	1050			2.
3.	Maximum Con't Rating (MCR), 1000 lb. stm./hr.	1000	675			3.
4.	Initial Year of Operation	1957, 1958, 1958	1949			4.
5.	Manufacturer	B&W	C. E.			5.
6.	Steam Temp., °F - Superheater/Reheater	1050 /1000	905 /	/	/	6.
7.	Design - Suction or Pressurized Furnace	S ___ P X	S X P ___	S ___ P ___	S ___ P ___	7.
8.	- Wet or Dry Bottom	W ___ D X	W ___ D X	W ___ D ___	W ___ D ___	8.
9.	- Furnace Volume, Cubic Feet	66,200	44,800			9.
10.	- Furnace Heating Surface, Sq. Ft.	16,000	10,800			10.
11.	Stack Number(2)	S-1, S-2, S-2	S-4			11.
12.	Stack Height/Diameter at Top, Feet	300,500,500 /20,25,25	300 / 22	/	/	12.
13.	Type of Firing(3) V,T,FW,S,Cy,HO,Tu	FW	T			13.
14.	Mixed Fuel(4), CF, SF	N.A.	N.A.			14.
15.	Oil: Steam or Mech Atomization(5)	St. ___ Me. B	St. N.A. Me. N.A.	St. ___ Me. ___	St. ___ Me. ___	15.
16.	Oil Pressure, PSI - Max.	1000	N.A.			16.
17.	Gas: Burner Design(5)	N.A.	B			17.
18.	Coal: Burner Design(5)	N.A.	B			18.
19.	Windbox Pressure Inches H2O (Full Load)	25	6.61			19.
20.	Flyash Reinjection(6)	No	No			20.
	Steam Temperature Control:					
21.	- Attemperation(6)	Yes	No			21.
22.	- Flue Gas Recirc., % Max. - Before/After Burner	B 0 A 7.5%	B 0 A 0	B ___ A ___	B ___ A ___	22.
23.	- Tilting Burners(6)	No	Yes			23.
24.	Two-Stage Combustion(6) (See Section II)	No	No			24.
25.	Boiler Efficiency-% (Full Load) Coal/Oil/Gas	-- / 88.5 / --	85.5 / -- / 81.0	/ /	/ /	25.

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(1) Please attach boiler outline sketch similar to attachments.

(2) Give plant stack designation and height of stack into which boiler discharges.

(3) Vertical, Tangential, Front-Wall, Stoker, Cyclone, Horizontally Opposed, Turbo Furnace.

(4) Combination Firing (Alternate Burners on Different Fuels), Simultaneous Firing (2 Fuels in Same Burner/s).

(5) See attached sketches. Indicate burner configuration similar to Sketch A, B, C. If different, indicate type and manufacturer.

(6) (Yes or No).

	FUEL DATA[7], Tons/Hr., bbl/hr., 1000 CF/hr.	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	
26.	Max. Con't Rating (Full Load)		182		32.8		938							26.
27.	3/4 Load		137		24.9		712							27.
28.	1/2 Load		92		17.0		487							28.
29.	Annual Consumption (1967) 1000 Tons, 1000 bbls., or 10^6 cu. ft.		960		54		1158							29.
30.	Av. Heat Content, BTU/lb., gal. or CF (Dry)		18,300		13,500		1010							30.
31.	Sulfur Content - Weight %[8]		2.2		1.6		0							31.
	OPERATING DATA													
32.	Flue Gas Rate - Full Load, 1000 lbs./hr.		1,370		910		920							32.
33.	" " " - 3/4 Load " " "		1,040		692		704							33.
34.	" " " - 1/2 Load " " "		720		473		480							34.
35.	Excess Air/O_2,% - Full Load	/	/2.0	/	20/	/	15/	/	/	/	/	/	/	35.
36.	" " " - 3/4 Load	/	/2.5	/	22/	/	16/	/	/	/	/	/	/	36.
37.	" " " - 1/2 Load	/	/3.0	/	24/	/	18/	/	/	/	/	/	/	37.
38.	NO_x Emissions, ppm[9] (Calc. to 3% O_2) - Full Ld.		750		850		700							38.
39.	" " " " " " " - 3/4 Ld.		600		640		585							39.
40.	" " " " " " " - 1/2 Ld.		480		500		430							40.
41.	No. of Burners - Full Load		12		8		8							41.
42.	" " " - 3/4 Load		12		8		8							42.
43.	" " " - 1/2 Load		6		4		4							43.
44.	Preheated Air Temp. °F		530		540		500							44.
45.	Burner Flame " "		2900		2750		2800							45.
46.	Flue Gas Entering Superheater " "		2150		2150		2200							46.
47.	Flue Gas Entering Economizer " "		975		1050		1075							47.
48.	Flue Gas Entering Air Preheater " "		730		750		760							48.
49.	Flue Gas Leaving Air Preheater " "		320		300		340							49.
50.	Oil Atomizing Temperature °F		220		N.A.		N.A.							50.
51.	Flue Gas Cleaning Equip.,[10] E,WS,Mech,Bag		N.A.		E		N.A.							51.
52.	Efficiency of Gas Cleaning Equipment - %		N.A.		97		N.A.							52.

	LOAD VARIATION (Number of Boiler Hours in Typical Week)	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	
53.	No Load	100	80	74	60					53.
54.	Less Than 40% Load									54.
55.	40-59% Load		20							55.
56.	60-79% Load	80	70							56.
57.	80-99% Load	40	60							57.
58.	Full Load	220	210	74	88					58.
	Total	444	444	148	148					

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(7) Assume single fuel firing.

(8) Please attach typical analysis of fuel (ultimate preferred), ash and flyash. Also include % of ash collected as flyash, % ash collected as bottom ash. If analysis data not readily available, please give name and address of supplier.

(9) Complete only if data are available from stack tests (also state method used for NO_x analysis).

(10) Electrostatic Precipitator, Wet Scrubber, Mechanical, Bag Filter.

9. BIBLIOGRAPHY

ATTACHMENT 4

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1950

United States

Fuel Sources	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (10^{12} BTU) Tons $NO_x/10^9$ Ft.^{3} Tons NO_x	1,568 (1,642) 58[2] 91,000	3,191 (3,302) 107[2] 341,000	629 (651) 195[2] 123,000	555,000		555,000
2. Liquefied Gases[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	54.4 (218) 12,000[3]	89 (522) 54,000[3]		66,000		66,000
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tonx NO_x	406.2 (2,385) 252[2] 102,000	266.4 (1641.7) 1,512[2] 402,000	106.3 (662.2) 2,184[2] 232,000	736,000	261 (1.145) 4,660[2] 1,216,000	2,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU) Tons $NO_x/10^6$ Tons Tons NO_x	110,422 (2,913) 4[2] 442,000	104,748 (3,108) 10[2] 1,047,000	91,871 (2,227) 10[2] 919,000	2,408,000		3,547,000
5. Refuse Burning[4] - 10^6 Tons Tons $NO_x/10^6$ Tons Tons NO_x	77 1,000[2] 77,000	33 1,000[2] 33,000		110,000		110,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x					984 (5,166) 2,373[2] 2,335,000	2,335,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x					6,000[5]	6,000
8. Total from Combustion - Tons NO_x	724,000	1,877,000	1,274,000	3,875,000	3,557,000	7,432,000

1. W. E. Morreson and C. L. Readling. An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calculated on a BTU basis using natural gas emission factor - i.e. (218/1642) x 91,000 = 12,000 Tons NO_x.
4. Calculated as 4# refuse per capita day (70% household and commercial - 30% industrial).
5. Assumed 20# NO_x per Flight. Used Resources for Future Inc. Estimate of Passenger-Miles.

ATTACHMENT 5

NO$_x$ EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1955

United States

Fuel Sources	Household and Commercial		Industrial		Electric Generation		Total Stationary Sources	Transportation		Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (10^{12} BTU)	2,753	(2,850)	4,419	(4,573)	1,153	(1,194)				
Tons NO$_x$/10^9 Ft.^{3}	58[2]		107[2]		195[2]					
Tons NO$_x$	160,000		473,000		225,000		858,000			858,000
2. Liquefied Gases[1] - 10^6 BBl (10^{12} BTU)	72	(288)	129	(749)						
Tons NO$_x$/10^6 BBl										
Tons NO$_x$	16,000[3]		82,000[3]				98,000			98,000
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU)	527	(3,098)	3,14	(1,925)	82	(512)		301	(1,824)	
Tons NO$_x$/10^6 BBl	252[2]		1,512[2]		2,184[2]			4,660[2]		
Tonx NO$_x$	133,000		475,000		179,000		787,000	1,403,000		2,190,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU)	66,039	(1,775)	101,976	(2,883)	143,759	(3,484)				
Tons NO$_x$/10^6 Tons	4[2]		10[2]		10[2]					
Tons NO$_x$	264,000		1,020,000		1,438,000		2,722,000			2,722,000
5. Refuse Burning[4] - 10^6 Tons	84		36							
Tons NO$_x$/10^6 Tons	1,000[2]		1,000[2]							
Tons NO$_x$			36,000				120,000			120,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU)								1,361	(7,143)	
Tons NO$_x$/10^6 BBl								2,373[2]		
Tons NO$_x$								3,230,000		3,230,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} BTU)										
Tons NO$_x$/10^6 BBl										
Tons NO$_x$								10,000[5]		10,000
8. Total from Combustion - Tons NO$_x$	657,000		2,086,000		1,842,000		4,585,000	4,643,000		9,228,000

1. W. F. Morreson and C. L. Readling. An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calculated on a BTU basis using a natural gas emission factor - i.e. (288/2850) x 160,000 = 16,000 Tons NO$_x$.
4. Calculated as 4# refuse per capita day (70% household and commercial - 30% industrial).
5. Assumed 20# NO$_x$ per Flight. Used Resources for Future Inc. Estimate of Passenger-Miles.

ATTACHMENT 6

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1960

United States

Fuel Sources	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (10^{12} BTU) Tons $NO_x/10^9$ Ft.^{3} Tons NO_x	4,123 (4,268) 58[2] 239,000	5,714 (5,915) 107[2] 611,000	1,724 (1,785) 195[2] 336,000	1,186,000		1,186,000
2. Liquefied Gases[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	101 (403) 22,600[3]	142 (816) 84,000[3]		106,600		106,600
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	642 (3,785) 252[2] 162,000	273 (1,858) 1,512[2] 412,000	90 (564) 2,184[2] 197,000	771,000	280 (1,693) 4,660[2] 1,310,000	2,081,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU) Tons $NO_x/10^6$ Tons Tons NO_x	37 (1,023) 4,000[2] 148,000	171 (4,767) 10,000[2] 1,710,000	177 (4,257) 10,000[2] 1,770,000	3,628,000		3,628,000
5. Refuse Burning[4] - 10^6 Tons Tons $NO_x/10^6$ Tons Tons NO_x	92 1,000[2] 92,000	39 1,000[2] 39,000		131,000		131,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	--	--	--	--	1,497 (7,854) 2,373[2] 3,552,000	3,552,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	--	--	--	--	136 (738) 9,200 [5]	9,200
8. Total from Combustion - Tons NO_x	663,600	2,856,000	2,303,000	5,822,600	4,871,200	10,693,800

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1. W. E. Morrison and C. L. Readling. An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calculated on a BTU basis using natural gas emission factor - i.e. (403/4268) x 239,000 = 22,600 tons.
4. Calculated as 4# refuse per capita day (70% household and commercial - 30% industrial).
5. Assumed 20# NO_x flight.', with 34.6 billion passenger miles (Resources for Future) and 37,000 estimated passenger miles per flight. results in 9,200 tons NO_x.

ATTACHMENT 7

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1965

United States

Fuel Source	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (10^{12} BTU) Tons $NO_x/10^9$ Ft.^{3} Tons NO_x	5,346 (5,534) 58[2] 310,000	7,142 (7,392) 107[2] 764,000	2,318 (2,399) 195[2] 452,000	1,526,000		1,526,000
2. Liquefied Gases[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	127 (511) 28,500[3]	154 (888) 92,000[3]		120,500		120,500
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x	716 (4,233) 252[2] 181,000	290 (1,778) 1,512[2] 439,000	119 (743) 2,184[2] 260,000	880,000	304 (1,823) 4,660[2] 1,417,000	2,297,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU) Tons $NO_x/10^6$ Tons Tons NO_x	22 (625) 4,000[2] 88,000	193 (5,539) 10,000[2] 1,930,000	245 (5,880) 10,000[2] 2,450,000	4,468,000		4,468,000
5. Refuse Burning[4] - 10^6 Tons Tons $NO_x/10^6$ Tons Tons NO_x	100 1,000[2] 100,000	42 1,000[2] 42,000		142,000		142,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x					1,720 (9,028) 2,373[2] 4,082,000	4,082,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} BTU) Tons $NO_x/10^6$ BBl Tons NO_x					221 (1,220) 10,300[5]	10,300
8. Total from Combustion - Tons NO_x	707,500	3,267,000	3,162,000	7,136,500	5,509,300	12,645,800

1. W. E. Morrison and C.L. Readling. An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calc. from Nat'l. Gas on a BTU Basis - i.e. (511/5534) x 310,000 = 28,500 Tons.
4. Calculated as 4# refuse per capita day (70% Household and Commercial - 30% Industrial).
5. Assumed 20# flight of NO_x ∴ with 49 billion passenger miles (Resources for Future Inc.) and 48,000 estimated passenger miles per flight results in 10,260 tons NO_x for 1965.

ATTACHMENT 9

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1970

United States

Fuel Source	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} $(1)^{12}$ BTU)	6,507 (6,735)	8,279 (8,531)	2,485 (2,572)			
Tons $NO_x/10^9$ Ft.^{3}	58[2]	107[2]	195[2]			
Tons NO_x	377,000	886,000	485,000	1,748,000		1,748,000
2. Liquefied Gases[1] - 10^6 BBl (10^{12} BTU)	177 (713)	179 (1,005)				
Tons $NO_x/10^6$ BBl						
Tons NO_x	40,000[3]	104,000[3]		144,000		144,000
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU)	700 (4,145)	328 (1,959)	124 (781)		383 (2,298)	
Tons $NO_x/10^6$ BBl	252[2]	1,512[2]	2,184[2]		4,660[2]	
Tons NO_x	176,000	496,000	271,000	943,000	1,785,000	2,728,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU)	17 (485)	185 (5,290)	321 (7,729)			
Tons $NO_x/10^6$ Tons	4,000[2]	10,000[2]	10,000			
Tons NO_x	68,000	1,850,000	3,210,000	5,128,000		5,128,000
5. Refuse Burning[4] - 10^6 Tons	10.	44				
Tons $NO_x/10^6$ Tons	1,000[2]	1,000[2]				
Tons NO_x	104,000	44,000		148,000		148,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU)					1,994 (10,465)	
Tons $NO_x/10^6$ BBl					2,373[2]	
Tons NO_x					4,730,000	4,730,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} BTU)					290 (1,602)	
Tons $NO_x/10^6$ BBl						
Tons NO_x					13,900[5]	13,900
8. Total from Combustion - Tons NO_x	765,000	3,380,000	3,966,000	8,111,000	6,528,900	14,639,900

1. W. E. Morrison and C. L. Readling. An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calc. from Nat'l. Gas on a BTU Basis - i.e.,(713/6,735) x 377 = 40,000 Tons
4. Calculated as 4# refuse per capita day (70% Household and Commercial + 30% Industrial).
5. Assumed 20# flight of NO_x

ATTACHMENT 9

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1975

United States

Fuel Source	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (10^{12} BTU)	7,913 (8,192)	9,507 (9,839)	2,664 (2,757)			
Tons $NO_x/10^9$ Ft.^{3}	58[2]	107[2]	195[2]			
Tons NO_x	459,000	1,017,000	519,000	1,995,000		1,995,000
2. Liquefied Gases[1] - 10^6 BBl (10^{12} BTU)	247.5 (996)	219 (1,182)				
Tons $NO_x/10^6$ BBl						
Tons NO_x	56,000[3]	122,000[3]		178,000		178,000
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU)	687 (4,074)	376 (2,237)	131 (820)		482 (2,897)	
Tons $NO_x/10^6$ BBl	252[2]	1,512[2]	2,184[2]		4,660[2]	
Tons NO_x	173,000	570,000	286,000	1,029,000	2,250,000	3,279,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU)	13 (377)	177 (5,052)	424 (10,175)			
Tons $NO_x/10^6$ Tons	4,000[2]	10,000[2]	10,000[2]			
Tons NO_x	52,000	1,770,000	4,240,000	6,062,000		6,062,000
5. Refuse Burning[4] - 10^6 Tons	109	47				
Tons $NO_x/10^6$ Tons	1,000[2]	1,000[2]				
Tons NO_x	109,000	47,000		156,000		156,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU)					2,312 (12,132)	
Tons $NO_x/10^6$ BBl					2,373[2]	
Tons NO_x					5,500,000	5,500,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} BTU)					380 (2,103)	
Tons $NO_x/10^6$ BBl						
Tons NO_x					18,000[5]	18,000
8. Total from Combustion - Tons NO_x	849,000	3,526,000	5,045,000	9,420,000	7,768,100	17,188,000

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1. W. E. Morrison and C. L. Readling. An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calc. from Nat'l. Gas on a BTU Basis
4. Calculated as 4# refuse per capita day (70% Household and Commercial - 30% Industrial).
5. Assumed 20# flight of NO_x

ATTACHMENT 10

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 1980

United States

Fuel Source	Household and Commercial	Industrial	Electric Generation	Total Stationary Sources	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (1 ^{12} BTU)	9,662 (10,000)	10,962 (11,305	2,874 (2,976)			
Tons $NO_x/10^9$ Ft.^{3}	58[2]	107[2]	195[2]			
Tons NO_x	560,000	1,173,000	560,000	2,293,000		2,293,000
2. Liquefied Gases[1] - 10^6 (10^{12} BTU)	343 (1,405)	285 (1,444)				
Tons $NO_x/10^6$ BBl						
Tons NO_x	79,000[3]	150,000[3]		229,000		229,000
3. Kero., Dist. & Resid.[1] - 10^6 BBl (10^{12} BTU)	679 (4,317)	433 (2,461)	137 (861)		607 (3,559)	
Tons $NO_x/10^6$ BBl	252[2]	1,512[2]	2,184[2]		4,660[2]	
Tons NO_x	171,009	655,000	299,000	1,125,000	2,820,000	3,945,000
4. Coal + Lignite[1] - 10^6 Tons (10^{12} BTU)	10 (325)	174 (5,665)	555 (13,319)			
Tons $NO_x/10^6$ Tons	4,000[2]	10,000	10,000[2]			
Tons NO_x	40,000	1,740,000	5,550,000	7,330,000		7,330,000
5. Refuse Burning[4] - 10^6 Tons	116	50				
Tons $NO_x/10^6$ Tons	1,000[2]	1,000[2]				
Tons NO_x	116,000	50,000		166,000		166,000
6. Gasoline[1] - 10^6 BBls (10^{12} BTU)					2,677 (14,050)	
Tons $NO_x/10^6$ BBl					2,373[2]	
Tons NO_x					6,350,000	6,350,000
7. Jet Fuel[1] - 10^6 BBl (10^{12} VTU)					502 (2,782)	
Tons $NO_x/10^6$ BBl						
Tons NO_x					23,000[5]	23,000
8. Total from Combustion - Tons NO_x	966,000	3,768,000	6,409,000	11,143,000	9,193,000	20,336,000

1. W. E. Morrison and C. L. Readling. An Energy Model for the United States, Featuring energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000. IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calc. from Nat'l. Gas on a BTU Basis
4. Calculated as 4# refuse per capita day (70% Household and Commercial + 30% Industrial).
5. Assumed 20# flight of NO_x

ATTACHMENT 11

NO_x EMISSIONS FROM COMBUSTION SOURCES FOR YEAR 2000

United States

Fuel Source	Household and Commercial	Industrial	Electric Generation[5]	Total Stationary	Transportation	Grand Total Stationary and Transportation
1. Natural Gas[1] - 10^9 Ft.^{3} (10^{12} BTU) Tons $NO_x/10^9$ Ft.^{3} Tons NO_x	18,475 (19,066) 58[2] 1,070,000	16,962 (17,504) 107[2] 1,810,000	4,000 (4,128) 195[2] 780,000	3,660,000		3,660,000
2. Coal and Lignite[1] - 10^6 Tons (10^{12} BTU) Tons $NO_x{}^2/10^6$ Tons Tons NO_x	-- --	76 (2,000) 10,000[2] 760,000	780 (18,720) 10,000[2] 7,800,000	8,560,000	-- --	8,560,000
3. Petroleum and Nat'l 10^6 BBl[1] (10^{12} BTU) Gas Liquids Tons $NO_x/10^6$ BBl Tons NO_x	318 (2,000) 252 [2] 80,000	548 (3,441) 1,512[2] 826,000	137 (861) 2,184[2] 299,000	1,205,000	6,627 (41,648) 2,790[4] 18,488,000	19,693,000
4. Refuse Burning[3] 10^6 Tons Tons $NO_x/10^6$ Tons Tons NO_x	300 1,000[2] 300,000	183 1,000[2] 183,000	--	483,000	--	483,000
Tons NO_x from Combustion	1,450,000	3,579,000	8,879,000	13,908,000	18,488,000	32,396,000

1. W. E. Morrison and C. L. Readling, An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000, IC 8384 - 1968 U.S. Dept. of Int. Bu. of Mines.
2. R. L. Duprey. Compilation of Air Pollutant Emission Factors, U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.
3. Calculated as 4 pounds refuse per capita-day (70% household and commercial, 30% industrial).
4. Weighed average emission factor from [2].
5. Assumes hydropower and nuclear power accounts for 68% of total power generation.

ATTACHMENT 12

UNCONTROLLED NO_x EMISSIONS - MILLIONS OF TONS FOR YEAR 1980 - MORPHOLOGICAL ANALYSIS

UTILITY-ELECTRIC GENERATION		INDUSTRIAL, HOUSEHOLD AND COMMERCIAL SECTORS											
		I-1 Conv'l. Combustion - Gas, Oil & Coal			I-2 Conv'l Combustion, Nat'l Gas Only			I-3 Fuel Cells - Nat'l Gas			I-4 Utility Electricity Only		
		Transportation			Transportation			Transportation			Transportation		
		T-1 Conv'l	T-2 El. Car	T-3 Fuel Cell	T-1	T-2	T-3	T-1	T-2	T-3	T-1	T-2	T-3
U-1 Conv'l. - Gas, Oil, Coal, Hydro & Nuclear	Stat'y.	11.1	23.4	11.1	9.7	22.0	9.7	0.2	9.4	0.2	33.6	45.9	25.7
	Transp.	9.2	0	0	9.2	0	0	9.2	0	0	9.2	0	0
	Total	20.3	23.4	11.1	18.9	22.0	9.7	9.4	9.4	0.2	42.8	45.9	25.7
U-2 Conv'l - Nat'l Gas Only	Stat'y.	9.5	16.0	9.5	8.1	14.6	8.1	0.2	6.7	0.2	19.4	25.9	19.4
	Transp.	9.2	0	0	9.2	0	0	9.2	0	0	9.2	0	0
	Total	18.7	16.0	9.5	17.3	14.6	8.1	9.4	6.7	0.2	28.6	25.9	19.4
U-3 Conv'l Coal Only	Stat'y.	14.5	27.6	14.5	13.1	26.2	13.1	0.2	13.3	0.2	39.5	52.6	39.5
	Transp.	9.2	0	0	9.2	0	0	9.2	0	0	9.2	0	0
	Total	23.7	27.6	14.5	22.3	26.2	13.1	9.4	13.3	0.2	48.7	52.6	39.5
U-4 Conv'l Fuel Oil Only	Stat'y.	13.7	26.0	13.7	12.3	24.6	12.3	0.2	12.5	0.2	36.4	48.9	36.4
	Transp.	9.2	0	0	9.2	0	0	9.2	0	0	9.2	0	0
	Total	22.9	26.0	13.7	21.5	24.6	12.3	9.4	12.5	0.2	45.6	48.9	36.4
U-5 Conv'l Nuclear Only	Stat'y.	4.7	4.7	4.7	3.3	3.3	3.3	0.2	0.2	0.2	0.2	0.2	0.2
	Transp.	9.2	0	0	9.2	0	0	9.2	0	0	9.2	0	0
	Total	13.9	4.7	4.7	12.5	3.3	3.3	9.4	0.2	0.2	9.4	0.2	0.2
U-6 Fuel Cells Nat'l Gas	Stat'y.	4.7	4.7	4.7	3.3	3.3	3.3	.2	0.2	0.2	0.2	0.2	0.2
	Transp.	9.2	0	0	9.2	0	0	9.2	0	0	9.2	0	0
	Total	13.9	4.7	4.7	12.5	3.3	3.3	9.4	0.2	0.2	9.4	0.2	0.2

ATTACHMENT 13

UNCONTROLLED NO_x EMISSIONS - MILLIONS OF TONS FOR YEAR 2000 - MORPHOLOGICAL ANALYSIS

UTILITY-ELECTRIC GENERATION		INDUSTRIAL, HOUSEHOLD AND COMMERCIAL SECTORS											
		I-1 Conv'l. Combustion - Gas, Oil & Coal			I-2 Conv'l Combustion, Nat'l Gas Only			I-3 Fuel Cells - Nat'l Gas			I-4 Utility Electricity Only		
		Transportation			Transportation			Transportation			Transportation		
		T-1 Conv'l	T-2 El. Car	T-3 Fuel Cell	T-1	T-2	T-3	T-1	T-2	T-3	T-1	T-2	T-3
U-1 Conv'l. - Gas, Oil, Coal, Hydro & Nuclear	Stat'y.	13.9	35.5	13.9	12.9	34.5	12.9	0	4.7	0	37.8	59.4	37.8
	Transp.	18.5	0	0	18.5	0	0	18.5	0	0	18.5	0	0
	Total	32.4	35.5	13.9	31.4	34.5	12.9	18.5	4.7	0	56.3	59.4	37.8
U-2 Conv'l - Fueled by Nat'l Gas Only	Stat'y.	19.3	31.1	19.3	18.4	30.2	18.4	0	11.8	0	29.6	41.4	29.6
	Transp.	18.5	0	0	18.5	0	0	18.5	0	0	18.5	0	0
	Total	37.8	31.1	19.3	36.9	30.2	18.4	18.5	11.8	0	48.1	41.4	29.6
U-3 Conv'l - Fueled by Coal Only	Stat'y.	33.8	57.4	33.8	32.7	56.4	32.7	0	23.7	0	59.4	83.1	59.4
	Transp.	18.5	0	0	18.5	0	0	18.5	0	0	18.5	0	0
	Total	52.3	57.4	33.8	51.2	56.4	32.7	18.5	23.7	0	77.9	83.1	59.4
U-4 Conv'l - Fueled by Fuel Oil Only	Stat'y.	32.1	54.5	32.1	31.1	53.5	31.1	0	22.4	0	56.1	78.5	56.1
	Transp.	18.5	0	0	18.5	0	0	18.5	0	0	18.5	0	0
	Total	50.6	54.5	32.1	49.6	53.5	31.1	18.5	22.4	0	74.6	78.5	56.1
U-5 Conv'l - Fueled by Nuclear Only	Stat'y.	5.0	5.0	5.0	4.0	4.0	4.0	0	0	0	0	0	0
	Transp.	18.5	0	0	18.5	0	0	18.5	0	0	18.5	0	0
	Total	23.5	5.0	5.0	22.5	4.0	4.0	18.5	0	0	18.5	0	0
U-6 Fuel Cells Only (Nat'l Gas)	Stat'y.	5.0	5.0	5.0	4.0	4.0	4.0	0	0	0	0	0	0
	Transp.	18.5	0	0	18.5	0	0	18.5	0	0	18.5	0	0
	Total	23.5	5.0	5.0	22.5	4.0	4.0	18.5	0	0	18.5	0	0

BIBLIOGRAPHY (PRELIMINARY 1/69)

NO_x Statistics and Forecasting

1. Aberbach, R. J, "While Hydro Generating Capacity Grows, Its Role in Total Picture Shrinks," Power, Oct. 67, S-12 - S-15.

2. American Petroleum Institute, "Petroleum Facts and Figures," 1967 ed.

3. Arakawa, Y. and Tanaka, Y., "New Developments in Methods of Forecasting Demand for Energy," World Power Conference, Tokyo Sectional Meeting, 1966.

4. Ayres, R. V., Selected Papers from the Hudson Institute on Technological Forecasting," hand written notes.

5. Barr, H. F., "Decline in Pollutants Forecast Despite Increasing Car Population," SAE J. 76, (May 1968): 42.

6. Bell, D., "Twelve Modes of Prediction," DAEDALUS, 1966.

7. Berman, P. A. and Stephens, J. O., "Advanced Combined Cycle Gas Turbines for Electrical Power Plants," Dyna (Madrid) 41 (11), 623-626 (Nov. 1966).

8. Blifford, I. H. and Meeker, G. O., "Factor Analysis Model of Large Scale Pollution," Atmospheric Environment v 1 n 2, March 1667, 147-57.

9. Bunyard, F. L. and Williams, J. D., "Interstate Air Pollution Study - St. Louis Area Air Pollutant Emissions Related to Actual Land Use," J. Air Poll. Control Assoc. 17, (4), 215-219 (Apr. 1967).

10. Burton, E. S., Peterkin, S. R. and Sanjour, W., "A Cost Effectiveness Approach to Urban Air Pollution Abatement," 1968 Joint National Meeting of the Operations Research Society of America and the Institute of Management Sciences, San Francisco, May 1968.

11. Census of Manufactures, "Fuels and Electric Energy Consumed in Manufacturing Industries," Department of Commerce, Washington, D.C., 1963.

12. Citron, M. J., "Forecasting Technology," International Science & Technology, September 1967, 83-92.

13. Citron, M. J., et al, "A Proposal for a Navy Technological Forecast," Parts I & II, 2 Vols., Headquarters, Naval Material Command, Washington, D.C., May 1, 1966 (AD 659-199) & (AD 659-200).

14. Citron, M. J., "Quantitative Utility Estimates for Science and Technology (QUEST)," IEEE Transactions on Engineering Management, Vol. EM-14, No. 1, March 1967, 51-62.

15. Citron, M. J., "Technological Forecasting Bibliography," (Partially Annotated), 457-474.

BIBLIOGRAPHY (PRELIMINARY 1/69)

16. Coleman, R., "The Outlook for Fertilizers," CEP, July 1968, 68-71.

17. Constance, J. A., "Systems Analysis for Industrial Air Problems," Air Eng., V 10 n 3, March 1968, 14-17.

18. Diehl, E. K, "Reduction of Emission of Oxides of Nitrogen for Present and Future Prospects," U.S. Public Health Serv. Publ. No. 1649, 179-82 (1966).

19. Dirkes, W. E. and Watts, A. A., "The Systems Approach to Forecasting," Missile and Space Div., General Electric Co.

20. Edison Electric Institute, Vennard, S., "Electricity in the City of the Year 2000.", EEI, April 17, 1967.

21. Edison Electric Institute, " Historical Statistics of the Electric Utility Industry," EEI Publication #62-69, 3M-4-62.

22. Edison Electric Institute, "Semi-Annual Electric Power Survey," for the following years: Oct. 1949, April 1950, Oct. 1950, April 1951, Oct. 1951, April 1952, Oct. 1952, April 1953, Oct. 1953, April 1954, Oct. 1954, Oct. 1955, Oct. 1956, April 1957, Oct. 1957, April 1958, Oct. 1958, April 1959, Oct. 1959, April 1960, Oct. 1960, April 1961, Oct. 1961, April 1962, Oct. 1962, April 1963, Oct. 1963, April 1964, Oct. 1964, April 1965, Oct. 1965, April 1966, Oct. 1966, April 1967, Oct. 1967, April 1968.

23. Edison Electric Institute, "43rd Semi-Annual Electric Power Survey," April 1968.

24. Edison Electric Institute, "Statistical Year Book of the Electric Utility" for: 1963 (published Sept. 1964), No. 31, Publication No. 64-43, 1964 (published Sept. 1965), No. 32, Publication No. 65-44, 1965 (published September 1966), No. 33, Publication No. 66-49, 1966 (published Sept. 1967), No. 34, Publication No. 67-26.

25. Edison Electric Institute, "The Year 2000," EEI 35, (9), Oct. 1967.

26. Edsall, M. S., "Analysis of Economic Factors in Catalytic Air Treatment," Air Engineering, (Oct. 1965), Reference in #68-177.

27. Electrical World - McGraw Hill Weekly, "1968 Annual Statistical Reports," Parts 1 & 2.

28. Electrical World - McGraw-Hill Weekly, "12th Annual Report on Nuclear Power," June 12, 1967.

BIBLIOGRAPHY (PRELIMINARY 1/69)

29. Electrical World - McGraw-Hill Weekly, "18th Annual Electrical Industry Forecast," Sept. 18, 1967.

30. Federal Power Commission, "National Power Survey," Part I, 296 pp., Part II, 423 pp.

31. Federal Power Commission, "Statistics of Privately Owned Electric Utilities in the United States," 1966.

32. Federal Power Commission, "Statistics of Publicly-owned Electric Utilities in the United States," 1966.

33. Federal Power Commission, "Steam-Electric Plant Construction Cost and Annual Production Expenses," 1949, 1950, 1951, 1953, 1954, 1956, 1957, 1958, 1961, 1962, 1963, 1966, 1967 (tables).

34. Galstann, L. S., Steigerwald, B. J., Ludwig, J. H. and Garrison, H. R., "What Does It Cost to Desulfurize Fuel Oil?" CEP (Chem. Eng. Progress) 61:49-58 (Sept. 1965).

35. Gilfillan, S. C., "The Prediction of Technical Change," The Review of Economics and Statistics, Vol. XXXIV, Nov. 1952, 368-385.

36. Glaser, P. E., "The Future of Power from the Sun," Power, August 1968, 61-3.

37. Harris, H. E., "Coke Making in the United States. The Future,", Can. Mining Met. Bull. 60 (665), 1038-40 (1967).

38. Haydon, B., "The Year 2000," March 1967, Obtained from the RAND Corp., Selected from Abstracts, Vol. 5 #3, Jan.-Sept. 1967. (This one superseded.)

39. Heller, A. N. and Walters, D. F., "Impact of Changing Patterns of Energy Use on Community Air Quality," J. Air Pollution Control Assoc., 15, 423-8 (1964).

40. Interdepartmental Energy Study, "Energy R&D and National Progress," Executive Office of the President, Office of Science and Technology, 1964, 437 pp.

41. Isenson, R. S., "Technological Forecasting - A Management Tool," Business Horizons, summer 1967, 37-45+.

42. Jantseh, E., "Forecasting the Future," Science Journal V3 #10, Oct. 1967, 40-45.

BIBLIOGRAPHY (PRELIMINARY 1/69)

43. Jantseh, E., "Technological Forecasting in Perspective," Organization for Economic Cooperation and Development, Paris France, 1967.

44. Jenkins, G. M. and Youle, P. V., "A Systems Approach to Management," O.R.Q. Special Conference Issue.

45. Jimeson, R. M., "The Economics of Utilizing Solvent Refined Coal in Powerplants," Presented at the Symposium on Economics of Air Pollution Control, 59th National Meeting of the Amer. Inst. Chem. Eng., Columbus, Ohio, May 15-18, 1966.

46. Kahn, H., "On Alternate World Futures," Selected Papers from the Hudson Institute.

47. Landsberg, H. H. and Schur, S. P., "Energy in the United States: Sources Uses, and Policy Issues," Random House, New York (168).

48. Landsberg, H. H. et al, "Resources in America's Future Patterns of Requirements and Availabilities, 1960-2000," The Johns Hopkins Press, Library of Congress, Cat. #63-7233.

49. Lenz, R. C. Jr., "Technological Forecasting," 2nd Ed., Aeronautical Systems, Div., AFSC, ASD-TDS-62-414, Wright-Patterson AFB, Ohio, June 1962, (AD 408085).

50. "Long-Range Forecasting and Planning," A Symposium held at the U.S. Air Force Academy, Colorado, Clearing House, U.S., Department of Commerce, Springfield, Va.

51. Mansfield, E. et al, "The Logistic Process: Tables of the Stochastic Epidemic Curve and Application," The J. of the Royal Statistical Soc., 1960, Graduate School of Industrial Administration, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1960.

52. Morrison, W. E., "The Energy Dilemma - Which Fuel, What Market, When?" Prepring #65K302, Soc. of Mining Engineerins of AIME. Presented at SME fall Meeting - Rocky Mountain Minerals Conf., Phoenix, Arizona, Oct. 7-9, 1965, 26 pp.

53. Morrison, W. E. and Readling, C. L., "An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections to the Years 1980 and 2000," Bureau of Mines Information Center.

54. Morrison, W. E., "Summary Energy Balances for the U.S.: Selected Years 1947-62," Bu. Mines Inf. Cent., 7242, 1964, 32 pp.

BIBLIOGRAPHY (PRELIMINARY 1/69)

55. Mottley, C. M., "Strategic Foresighting," Contribution to a Discussion of Forecasting Techniques at Industrial Management Center Conference on Technological Forecasting for Industry, May 22-23, 1967, 8 pp.

56. National Academy of Sciences, National Research Council, Washington, D.C., "Waste Management and Control," a report of the Federal Council for Science and Technology by the Committee on Pollution, National Academy of Sciences.

57. National Coal Association, "Bituminous Coal Data," 1967.

58. National Coal Association, "Bituminous Coal Facts," 1968.

58.. National Coal Association, "Steam-Electric Plant Fuel Consumption and Costs," 1960, 1952, 1953, 1954, 1955, 1957.

60. National Coal Association, "Steam-Electric Plant Factors," 1956, 1957, 1958, 1959, 1960, 1961, 1962, 1963, 1964, 1965, 1966.

61. National Coal Association, "Steam-Electric Plant Factors, 1966," an annual study by the Division of Economics and Statistics.

62. National Coal Association, "Office of Coal Research 1968," Annual.

63. Nilsen, J., "Air Pollution - Costly to Ignore, Costly to Control," Chem. Eng. v 73 n, July 18, 1966, 90-2.

64. Patteson, N. T., "Fuels Consumed at Steam-Electric Plants 1955-1964."

65. Prehoda, R. W., "The Future and Technological Forecasting," pre-publication manuscript expected to be published in the U.S. in 1968.

66. Ridker, R. G., "Economic Costs of AP," published by F. A. Praeger, 1967.

67. Ritchings, F. A., "Raw Energy Resources for Electric Energy Generation," 1968 American Power Conference.

68. Rohrman, F. A., Steigerwald, B. J., Ludwig, J. H., "Next 30 Years," Power v 111 n 5, May 1967, 82-3.

69. Schon, D. etal, "The Role of the Federal Government in Technological Forecasting," Interagency Task Group on Technological Forecasting in Federal Government, January 1966.

70. SRI -"U.S. Electric Power Industry", Long Range Planning Service Report #321, May 1967.

BIBLIOGRAPHY (PRELIMINARY 1/69)

71. SRI Long Range Planning, "Air Pollution Control," Research Report #353, August 1968.

72. Spenser, M. H., "Business and Economic Forecasting: An Econometric Approach," Richard D. Irwin, Inc., Homewood, Ill., 1961, 412 pp.

73. Std. Oil Co. (N.J.), "World-Wide Long-Range Energy Forecast," Private Communication.

74. Statistical Abstracts of the U.S. 1953-1964, Section on Chemical Products, Bureau of the Census, U.S. Department of Commerce, reference taken from P.H.S.P. #999-AP-27, Atmospheric Emissions from HNO_3 Manufacturing Process.

75. SRI,"Coal," Long-Range Planning Service, Rept. #319, May 1967.

76. Swager, W. L., "Industrial Implications of Technological Forecasting," Paper presented to the 4th Symposium of the Engineer-Economy Division of the Am. Soc. for Engineering Education in Chicago, Ill., June 19, 1965, Battelle Memorial Institute.

77. Sweet, A. H. et al, "Need for a Pollution-free Vehicle," J. APCA v 18 #2 February 1968, 111-113.

78. Swager, W. L., "Technological Forecasting for Practical Planning," Petroleum Management, July 1966.

79. Sweezy, E. E., "Technological Forecasting - Principles and Techniques," paper presented at the 4th Symposium of the Eng. Economy Division, the Am. Soc. for Engineering Education, Chicago, Ill., June 19, 1965.

80. "Techniques Employed in Forecasting A.P.," Air Eng. v 8 n 10 October 1966, 22-3.

81. "Technological Forecasting," Report on Interservice ad hoc Study Group Sponsored by the Army Material Command, the Navy Material Command, and the Air force Command, June 30, 1967, available from the Department of Defense, Documentation Center, Cameron Station, Alexandria, Virginia.

82. Terrill, J. G., Harward, E. D. and Leggett I. P., "Environmental Aspects of Nuclear and Conventional Power Plants," Ind. Med. Surg., 36(6), 412-19 (June 1967).

83. Teitelbaum, P. D., "Energy Production and Consumption in the U.S.: An Analytical Study Based on 1954 Data," Bureau of Mines Rept. of Inv., 5821, 1961, 145 pp.

84. Vogely, W. A., "Patterns of Energy Consumption in the U.S.," Paper in General Papers, preprint Volume 149 at Mtg. American Chem. Soc., Division of Fuel Chemistry, Symposium of Fuel and Energy Economics, Detroit, Michigan, April 4-9, 1965, 205-221.

BIBLIOGRAPHY (PRELIMINARY 1/69)

85. Vogely, W. A., "Patterns of U.S. Energy Consumption to 1980," IEEE Spectrum, V. 4 #9. September 1967, 81-86.

86. Vogely, W. A., "Models of All-Gas and All-Electric Economics," Presented at 7th Biennial Gas Dynamics Symposium, August 23-25, 1967, 26 pp.

87. Vogely, W. A., "Patterns of Energy Consumption in the U.S., 1947 to 1965 and 1980 Projected," Preprint paper 83, 1A, World Power Conference, Tokyo, Japan, October 16-20, 1966, 24 pp.

88. Young, J. F., "Forecast of the Energy Future," for 1965 American Power Conference by Atomic Products Division, General Electric Co.

NO_x Removal from Stack Gases

100. Addison, C. C. and Lewis, J., "The Chemistry of the Nitrosyl Group (NO)," Quarterly Reviews, Chem. Soc. London, V. 9, 1955, 115-149.

101. Addison, C. C., "The Liquid Dinitrogen Tetroxide Solvent System, Part XIV," J. Chem. Soc., 1953, 1874-1879.

102. Addison, W. E., et al, "Sorption and Reactivity of N_2O and NO in Crystalline and Amorphous Silicious Sorbents," J. Chem. Soc., 757-769, 1955.

103. Air Pollution in L.A. or A.P. Data for L.A. County, January 1968.

104. Andersen, H. C., Green, W. J. and Steele, D. R., "Catalytic Treatment of HNO_3 Plant Tail Gas," Ind. & Eng. Chem. 53:199-204, March 1961.

105. Andersen, H. C., "Industrial Gas Purification with Noble Metal Catalysts," Dechema Monograph. 40, No. 616-641, 325-33 (1962).

106. Andersen, H. C., et al, U.S. Patent #2,970,034, "Method of Purifying Gases Containing Oxygen and Oxides of Nitrogen," Filed April 5, 1957, Patented January 31, 1961.

107. Andersen, H. C. and Keith, C. D., U.S. Patent #3,008,796, "Method of Purifying Gases Containing Oxygen and Oxides of Nitrogen," Filed June 6, 1958.

108. Andersen, H. C., et al, U.S. Patent #3,098,712, "Method for Selective Removal of Oxygen from Gaseous Mixtures of Oxygen and Nitric Oxide," Filed December 29, 1959, Patented July 23, 1963.

BIBLIOGRAPHY (PRELIMINARY 1/69)

109. Andersen, H. C., et al, "A New Family of Catalysts for Nitric Acid Tail Gases," Air Pollution Control Center.

110. Andersen, H. C. and Steele, D. R., "The Purification of Coke-Oven Gases with Platinum-Metal Catalysts," Engelhard Inds., Inc., Tech. Bull. 1, 106-8 (1960).

111. Andersen, H. C., et al, U.S. Patent #3,032,387, "Selective Removal of Nitrogen Oxides from Gas Streams," Filed April 17, 1959, Patented May 1, 1962.

112. Andersen, H. C., et al, U.S. Patent #3,084,023, "Treatment of Gases," Filed March 11, 1960, Patented April 2, 1963.

113. Androssow, L., "Uber die Katalytische Stickoxyd - Reduktion und Ammoniak - Oxydation (IV)," Jahrg. 60, 536-540, 1927.

114. Anon, "Where Tail Gas Oxidation Stands Today," Chem. Eng. 66, 66-68, January 12, 1959.

115. Ashmore, P. G., et al, "Reaction of Nitric Oxide and Oxygen," Trans. Faraday Soc. 58, 685 (1962).

116. "Atmospheric Emissions from Thermal Process Phosphoric Acid Manufacturing," Coop. Study Project - Manuf. Chemists Assoc., Inc., & PHS National Center for Air Pollution Control, Cincinnati, Ohio, 1967.

117. Atomics International - North American Rockwell Corp. Monthly Progress Report, Dec. 1, 1968 to January 1, 1969. "Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases," Contract PH 86-67-128.

118. Atsakawa, M., et al, "Study on the Removal of Nitrogen Oxide from Effluent Stack Gases," Tech. Rev. Mitsubishi Heavy Ind. 5 (2), 129 (1968).

119. Atroshchenko, V. I. and Kaut, V. M., "Kinetics of Absorption of Nitrogen Oxides by Concentrated Nitric Acid," Zhur. Priklad. Khim. 31, 352-60 (1958).

120. Atroshchenko, V. I., Goucharcuko, G. K. and Sedasheva, S. G., "Kinetics of Absorption of Nitrogen Dioxide by Solid Calcium Oxide," Khim. Prom., Inform. Nauk.-Tekhn. Zb. 1965 (1), 27-9.

121. Atroshchenko, V. I. and Karagin, S. N., "Nitric Acid Techniques," State Chem. Press, 1949.

BIBLIOGRAPHY (PRELIMINARY 1/69)

122. Atroshchenko, V. I., et al, "Rate of NO_x Absorption by Alkaline Solutions and by Nitric Acid," Air Pollution and Related Occupational Diseases, Vol 6, 299 pp., April 1961.

123. Atroshchenko, V. I., Tseitlin, A. N., Zasorin, A. P. and Zolotarev, V. S., "Recovery of Nitrogen Oxides from the Waste Effluents of Some Industries," Khim. Prom. 1960, Vol. 1, 79-80

124. Ayen, R. J. and Peters, M. S., "Catalytic Reduction of NO," Ind. Eng. Chem. Process Design Develop. 1, No. 3, 204-7 (1962).

125. Ayen, R. J. and Ng, Yu-Sim, "Catalytic Reduction of Nitric Oxide by Carbon Monoxide," Air Water Pollution 10, (1), 1-13 (1966).

126. Bachman, P. W. and Taylor, G. G., "Decomposition of Nitric Oxide by Platinum at Elevated Temperatures and Its Retardation by Oxygen," J. Phys. Chem. 33, 447 (1929).

127. Baker, R. A. and Doerr, R. C., "Catalytic Reduction of Nitrogen Oxides in Automobile Exhaust," J. Air Pollution Control Assoc. 14, (10), 409-14 (1964).

128. Baker, R. A. and Doerr, R. C., "Catalyzed Nitric Oxide Reduction with Carbon Monoxide," Ind. Eng. Chem., Process Design Develop. 4, (2), 188-91, (1965).

129. Baker, R. W., et al, "Catalytic Oxidation of NO on SiO_2," Chem. Eng. Progress Sym. Series, #4, Vol. 48, 1952, 103-9.

130. Baranov, A. V. and Okhramovich, A. E., "The Desorption of Nitrogen Oxides from Activated Carbon," Nauchn. Tr. Dnepropetr. Khim. Tekhnol. Inst. 1961, No. 12, Pt. 2, 185-8.

131. Barnes, E., "The Action of Nitric Oxide on Alkaline Hydroxides," J. Chem. Soc., 1931, 2605-20.

132. Barrer, R. M., et al, U.S. Patent #2,853,365, "Disproportionation of Nitric Oxides Using Crystalline Zeolites as Catalysts," Filed February 7, 1955.

133. Baxter, W. A., "Recent Electrostatic Precipitator Experience with Ammonia Conditioning of Power Boiler Flue Gases," Journal of APCA, Vol. 18, No. 12, December 1968.

134. Bedjai, G., Orbach, H. K. and Riesenfeld, F. C., "Reaction of Nitric Oxide with Activated Carbon and Hydrogen," Ind. Eng. Chem. 50, 1165-8, (1958).

135. Bent, F. A., U.S. Patent #1,888,547, "Process for the Removal of Nitric Oxide from Gases," Filed May 14, 1931, Patented November 22, 1932.

BIBLIOGRAPHY (PRELIMINARY 1/69)

136. Berning, R. E., et al, Volunteer Ordnance Works. Project No. 56-151, April, 1957.

137. Bethell, K. D., Shaw, J. T. and Thomas, A. C., "An Improved Form of Solid Oxidizer for the Conversion of Nitric Oxide to Nitrogen Dioxide in a Flow System," Chem. Ind. (London) 1968, (3), 91.

138. Betz, E. C. and Feist, H. J., "Catalytic Afterburning of Industrial Exhaust Gases," Technik. (Berlin) 20, (6) 395-401 (1965).

139. Beutner, H. P., et al, "Feasibility of a Regenerative High Temperature Amine Absorption Process for the Control of SO_2 Emissions from Stack Gases," Report from Arthur D. Little Inc. Prepared under NAPCA Contract PH 86-68-57, Aug. 1968.

140. Bienstock, D., et al, "Evaluation of Dry Processes for Removing Sulfur Dioxide from Power Plant Flue Gas," Journal of the Air Pollution Control Assoc. 5 (10), 459 (1965).

141. Bodenstein, M., "Vecocity of Reaction between Nitric Oxide and Oxygen," Z. Elektrochem. 24, 183-201 (1918); J. Soc. Chem. Ind. 37, 504A.

142. Breic, B. S., Dobenik, D. and Golic. L., "The Reaction of Nitrogen Oxides with Calcium Oxide," Monatsh. 94, (6), 1145-53 (1963).

143. Brennan, J. A., U.S. Patent #3,015,369, "Removal of Nitrogen Oxides from Combustion Gases," Filed May 23, 1960.

144. Briner, E., Lunge, G. H. and van der Wijk, A., "Reaction between Nitrogen Peroxide and Sulfur Dioxide," Helv. Chim. Acta 11, 1125-44 (1928).

145. Burdick, C. L., "Oxidation of Nitric Oxide and Its Catalysts," J. Am. Chem. Soc. 44, 244-51 (1922).

146. Bylov, V. D., Znamenskii, U. D., Kapitonova, L. P., and Shchedrov, M. S., "Scrubbing Nitrogen Oxides from Partially Oxidized Gases with Sulfuric Acid," Zu. Prikl. Khim. 35, 1503-5 (1962).

147. "(The) Calculation of Atmospheric Dispersion from a Stack," A CONCAWE Publication, 1966, 57 pp.

148. Carlton-Jones, D. and Schneider, H. B., "Tall Chimneys," Chem. Eng. 75, (22), 166-9 (October 14, 1968).

149. Caudle, P. G. and Denbigh, K. G., "Kinetics of the Absorption of Nitrogen Peroxide into Water and Aqueous Solutions," Trans. Faraday Soc. 49, 39-52 (1953).

150. Chaikivsky, M. and Siegmund, C. W., "Low Excess Air Combustion of Heavy Fuel-High Temperature Deposits and Corrosion," ASME Paper 64-WA/CD-2, New York City, 1964.

BIBLIOGRAPHY (PRELIMINARY 1/69)

151. Chambers, F. S. and Sherwood, T. K., "Absorption of Nitrogen Dioxides by Aqueous Solutions," Industrial and Engineering Chemistry, Vol. 29, No. 12, December 1955.

152. Childers, E., et al, U.S. Patent #3,125,408, "Method of Removing Nitrogen Oxides from Gases," Filed December 19, 1955, Patented March 17, 1964.

153. Childers, E., et al, U.S. Patent #2,910,343, "Process for Catalytically Reducing Nitrogen Oxides in Industrial Stack Gases," Filed December 8, 1955, Patented October 27, 1959.

154. Chu, C. and Hougen, O. A., "Optimum Design of a Catalytic Nitric Oxide Reactor," Chem. Eng. Progr. 57, No. 6, 51-8 (1961).

155. Coates, J. E., et al, "The Rate or Combination of Gaseous Nitric Oxide and Chlorine, Part I," J. Chem. Soc. Vol. 105, 2444-2452, 1914.

156. Cohn, J., Steele, D. R. and Anderson, H. C., U.S. Patent #2,975,025, "Selective Removal of Nitrogen Oxides from Oxygen-Containing Gases, Especially from Nitric Acid Production from Ammonia," March 14, 1961.

157. Cohn, J. G. E., U.S. Patent #3,118,727, "Method of Removing Nitrogen Oxides from Gases," Filed October 12, 1956.

158. Cronan, C. S., "Process & Technology - Where Tail Gas Oxidation Stands Today," Chem. Engineering, January 12, 1959.

159. Cuffe, S. T., "Catalyst Regeneration," Air Pollution Engineering Manual.

160. Daniels, F., et al, U.S. Patent #2,518,674, "Nitric Oxide Recovery System," Filed March 28, 1949.

161. Daniels, F., "Nitrogen Oxides and Development of Chemical Kinetics," Chem. & Eng. News, v 33, 1955, 2370-2373.

162. Danielson, J. A., "Air Pollution Engineering Manual," PHSP 999-AP-40, 1967.

163. Darley, E. F., Burleson, F. R., Mateer, E. H., Middleton, J. T. and Osterli, V. P., "Contribution of Burning of Agricultural Wastes to Photochemical Air Pollution," J. Air Pollut. Contr. Ass. 16, (12), 085-90 (1966).

164. Decker, L. D., "Incineration Techniques for Controlling Emissions of Nitrogen Oxides," UOP Air Correction Division, Greenwich, Connecticut, Paper No. 67-148.

165. Dols, M. J., Hock, B. and Oven, K., "Removal of Nitric Oxide from Coke-oven Gas," Dechema Monograph. 48, 835-858, 131-44 (1963).

BIBLIOGRAPHY (PRELIMINARY (1/69)

166. Donahue, J. L., "System Designs for the Catalytic Decomposition of Nitrogen Oxides," J. Air Pollution Control Assoc. 8, 209-12, 222 (1958).

167. Dunnicliff, H. B., et al, "The Interaction Between Nitric Oxide and Hydrogen Sulphide in the Presence of Water," J. Phys. Chem., 1931, 35, 1721-34.

168. DuPont, British Patent 799,159 (1958).

169. Ehnert, W., "Behavior of NO in Electrostatic Gas Purification," Brennstoff-Chem. 47 (9), 273-4 (1966).

170. Ergdahl, R. B., et al, "A Study of Effluents from Domestic Gas Fired Incinerators," American Gas Association, June 1959.

171. Ermenc, E. D., "Wisconsin Process System for Recovery of Dilute Oxides of Nitrogen," Chem. Eng. Progr. 52, 488-92 (1956).

172. Ermenc, E. D., "Wisconsin Process System for Recovery of Dilute Oxides of Nitrogen," Chem. Eng. Prog., Vol. 52 #11, November 1956. (Duplicate)

173. Feist, J., "The Catalytic Reduction of Nitrous Gases during the Manufacutre of Nitric Acid," Int. Clean Air Congr., Proc., London (1966), Part 1, 199-202.

174. Fenimore, C. P. and Jones, G. W., "Nitric Oxide Decomposition at 2200-2400°K," J. Phys. Chem. 61, 654-7 (1957).

175. Feustel, K., U.S. Patent 2,992,895, "Process for Recovering Oxides of Nitrogen and Sulfur from Gaseous Mixtures," Filed U.S. Patent Office March 4, 1958. Filed in Germany August 28, 1957

176. Fletcher, W., "Treatment of Nitric Acid Plant Tail Gas." Brit. Chem. Eng. 5, 780-90 (1960).

177. Foerster, F., Bowchardt, T. and Fricke, E., "Manufacture of Concentrated Nitric Acid from Nitrous Gases," Z. Angew. Chem. 33, I, 113-7, 129-32 (1920).

178. Fohl, T., "Optimization of Flow for Forcing Stack Wastes to High Altitudes," Air Pollution Control Assn. J v 17 n November 11, 1967, 730-733.

179. Foster, E. G. and Daniels, F., "Recovery of Nitrogen Oxides by Silica Gel," Industrial & Engineering Chemistry, Vol. 43, No. 4, April 1951.

180. Frankenberg, T. T. and Perry, H., "Air Pollution from Power Plants and Its Control," Combustion, v 34 n, February 8, 1963.

181. Fraser, J. M. and Daniels, F., "The Heterogeneous Decomposition of Nitric Oxide with Oxide Catalysts," J. Phys. Chem. 62, 215-20 (1958).

BIBLIOGRAPHY (PRELIMINARY 1/69)

182. Ganz, S. N., "Absorption of NO_x by Alumosilicates," 2nd Report, CFSTI: TT61-21982, APTIC #10161. (See J. Prikl. Khim. 31, 360-68 (1958).

183. Ganz, S. N. and Mamon, L. I., "Absorption of Nitric Oxide By Ferrous Sulfate," 1953, Translation Received from NAPCA.

184. Ganz, S. N. and Kuznetsov, I. E., "Alkaline Absorption of Oxides of Nitrogen in a Hollow Equiflow Tower with a Centrifugal Volume Sprayer. II," Tr. Dnepropetr. Khim.-Tekhnol. Inst., (16), 17-26 (1963).

185. Ganz, S. N. and Lokshin, M. A., "Effect of Basic Physicochemical Factors on the Rate of Absorption of Nitrogen Oxides by Solutions of $Ca(OH)_2$ in a Rapidly Revolving Absorber. II," Priklad. Khim. 30, 1525-35 (1957).

186. Ganz, S. N., "Kinetics of Absorption of Nitrogen Oxides by Sulfuric Acid in a Rapidly Revolving Absorber," J. Appl. Chem. U.S.S.R. 29, 1107-16 (1956).

187. Ganz, S. N. and Mamon, L. I., "Kinetics of Film Absorption of Nitric Oxide by Ferrous Sulfate," Zhur. Priklad. Khim. 30, 369-79 (1957).

188. Ganz, S. N., Luk'yanitsa, A. I. and Bel'china, L. A., "Production of Nitrogen-Iron Fertilizers from Waste Pickling Solutions. II. Combination of Pickling Solutions and the Purification of Gases from Nitrogen Oxides," Zh. Prikl. Khim. 37, (7), 1609-11 (1964).

189. Ganz, S. N. and Kravchinskaya, S. B., "Rate of Absorption of Nitrogen Oxides by Solutions of $Ca(OH)_2$ in a Revolving Absorber," Zhur. Priklad. Khim. 28, 145-55 (1955); J. Appl. Chem. (USSR) 28, 133-41 (1955)(transl.).

190. Ganz, S. N., "Sorption of NO_x by Solid Sorbents," J. Prikl. Khim. 31, 138-40 (1958); C.A. 52:9534.

191. "Gaseous Tracer Systems Developed by PHS," J. APCA v 18 #2, February, 1968.

192. Gehlen, H., "Reactions and Properties of Nitric Oxide and Its Compounds. I. The Action of Nitric Oxide on Sodium Hyposulfite," Ber. 64B, 1267-76 (1931).

193. Gehlen, H., "Reactions and Properties of Nitric Oxide and Its Compounds. II. The Salts of the Nitric Oxide Compound of Sulfurous Acid," Ber. 65B, 1130-40 (1932).

194. Gehlen, H., "Reactions and Properties of Nitric Oxide and Its Compounds. III. The Reaction Between Nitric Oxide and the Alkali Salts of Nitrosodisulfonic Acid," Ber. B66, 292-7 (1933).

195. Gerstle, R. W. and Peterson, R. F., "Atmospheric Emissions from Nitric Acid Manufacturing Processes," U.S. Public Health Serv. Publ. No. 999-AP-27, 89 pp. (1966).

BIBLIOGRAPHY (PRELIMINARY 1/69)

196. Gerstle, R. W. and Peterson, R. F., "Control of Nitrogen Oxide Emissions from Nitric Acid Manufacturing Processes," Air Eng. 9, (4), 24-8, 34 (1967).

197. Gillham, W. F., Martin, A. and Barber, F. R., "Sulfur Dioxide Concentrations Measured around a Modern Power Station," Int. Clean Air Congr., Proc., London, 1966 (Pt. 1), 185-7.

198. Giona, A. R. and Szepesy, L., "Elimination of Trace Amounts of Nitric Oxide by Adsorption," Magy. Kem. Folyoirat 71 (9), 399-403 (1965).

199. Gorfunkel, V. E. and Kil'man, Y. I., "Preparation of Solutions of Calcium Nitrite-Nitrate by Absorption of Nitrogen Oxides from Nitrose Gas Tailing with Milk of Lime," Trudy Gosudarst. Nauch.-Issledovatel. i Prockt. Inst. Azot. Prom. 1956, No. 5, 261-82; Referat. Zhur., Khim. 1958.

200. Gotaas, Y., "Dispersion of Atmospheric Pollutants," Tek. Ukebl. 114, (12), 212-16 (1967).

201. Grafe, K., "Calculated Versus Continuously Measured SO_2 Concentrations with Regard to Minimum Stack Heights and Urban Renewal," Intern. Clean Air Congr. Proc. I. 256-8, October 1966.

202. Grant, H. O., "Pollution Control in a Phosphoric Acid Plant," Chem. Eng. Prog. 60: #1, January 1964, 53-55.

203. Green, T. E. and Hinshelwood, C. N., "The Catalytic Decomposition of Nitric Oxide at the Surface of Platinum," J. Chem. Soc. 1709 (1966).

204. Greig, J. D. and Hall, P. G., "Thermal Oxidation of Nitric Oxide at Low Concentrations," Trans. Faraday Soc. 63, (3) 655-61 (1967).

205. Grosspietsel, H., et al, "Process for Removing Nitric Oxide from Gases Containing Unsaturated Hydrocarbons," (U.S. Patent #3,192,009).

206. Gruson, G. and Hanke, E., "Nitrogen Oxide Removal in Electrofilter Operation," Freiberg. Forschungsh, A No. 413, 37-73 (1967).

207. Haagen -Smit, A. J., "Progress Reports of Southern California Edison Tests on Removal of Sulfur Oxides & Nitrogen Oxides from Flue Gas," privately communicated.

208. Haagen-Smit, A. J.,"Removal of Particulate and Gaseous Contaminants from Power Plant Flue Gases," Proc Tech. Meeting West Coast Sect., Air Pollution Control Assoc., 1st, Los Angeles, 1957.

209. Halitsky, J., "Diffusion of Vented Gas around Buildings," Paper #61-35 at 54th Meeting of APCA, N.Y.C., June, 1961.

BIBLIOGRAPHY (PRELIMINARY 1/69)

210. Hasche, R. L., et al, "Studies on the Rate of Oxidation of NO. II. The Velocity of the Reaction Between NO and NO and O at 0° and 30°," J. Am. Chem. Soc., 47, 1207, 1925.

211. Haseba, S., et al, "Nitric Oxide Explosion," Chem. Engineering Progress, Vol. 62 #4, 92-96 (1966).

212. Hollaender, E., "Reduction of Nitrogen Oxides by Charcoal," Chem. Prumysl 15, (8), 498-500 (1965).

213. Hollings, H., "The Formation of Nitrogenous Gum during the Storage and Distribution of Gas," Gas Journal, November 11, 1936, 459-464.

214. Howard, C. S. and Daniels, F., "Stability of Nitric Oxide Over a Long Time Interval," J. Phys. Chem. 62, 360 (1958).

215. Hunter, J. B., "Platinum Catalysts and A.P. Control," S. Afr. Min. Engng. J. 438-440 (February 23, 1968).

216. Ioshpa, I. E., "Kinetics of Absorption of Nitrogen Dioxide by a Sulfuric Acid-Nitric Acid Mixture," Khim. Tekhnol. Miner. Udobr. (Tashkent: Fan) 1966, 74-81.

217. "Incinerator Spews Superclean Exhaust," Chemical Eng., January 3, 1968.

218. James, I. J., U.S. Patent #2,756,127, "Chemical Oxidation Process in the Adsorbed Phase," Filed June 30, 1952.

219. James, I. A., U.S. Patent #2,568,396, "Process for Producing and Separating Nitrogen Oxides," Filed July 19, 1946.

220. Janaf Thermochemical Tables, Prepared by the Dow Chemical Co. under Air Force Contract AF 04(611)7554.

221. Janiczek, W., "Verification of the Kinetics of Nitrogen Oxide Oxidation during Simultaneous Alkaline Absorption in Full-Scale Apparatus," Przemysl Chem. 37, 448-50 (1958).

222. Jeffins, G. C., "Effect of Operating Variables on the Stack Emission from a Modern Power Stationary Boiler," Paper presented at Am. Soc. of Mech. Engineers, Atlantic City, November-December, 1959.

223. Jeitner, O. and Konig, K., "The Elimination of Nitrous Gas Emission by Catalytic Reduction," Chem. Tech., 1967.

224. Johnston, H. S., et al, "Kinetics of Fast Gas Phase Reaction Between Ozone and NO," J. Chem. Phys. 22, 689, 1954.

225. Johnston, H. S., et al, "Kinetics of Rapid Gas Reaction Between Ozone and NO_2," J. Chem. Phys. 17, 386, 1949.

BIBLIOGRAPHY (PRELIMINARY 1/69)

226. Jordon, C. W., et al, "Gum Deposits in Gas Distribution Systems," Ind. & Eng. Chem. 26, 947-955, 1028-1038 (1934).

227. Jordan, C. W., et al, "Gum Deposits in Gas Distribution Systems - Adsorption of Nitric Oxide," Ind. & Eng. Chem., Vol. 27, #10, October 1935, 1180-1190.

228. Kakabadze, V. M. and Kakabadze, I. L., "Absorption of Nitrous Gases in a Dry Method, with Simultaneous Production of Mixed Fertilizers," Soobshcheniya Akad. Nauk Gruzin. S.S.R. 18, No. 5, 549-56 (1957).

229. Karivat, E., U.S. Patent #3,149,907, "Removal of Nitric Oxide from Gas Mixtures Containing the Same," Filed U.S. Patent Office August 11, 1968.

230. Kaufman, F. and Kelan, J. R., "Kinetics of Decomposition of NO," J. Chem. Phys., Vol. 21, 751, 1953.

231. Kerns, B. A., "Chemical Suppression of Nitrogen Oxides," Ind. Eng. Chem., Process Design Develop. 4, (3), 263-5 (1965).

232. Kircher, O. and Hougen, O. A., "Effect of Water Vapor on the Catalytic Oxidation of Nitric Oxide," A.I.Ch.E. Journal 3, 331-5 (1957).

233. Kobakhidze, A. G., "The Use of Managanese Carbonate Ores in the Chemical Industry, "Trudy Gruzin. Politekh. Inst. 1957, No. 6, 89-97.

234. Kobe, K. A., Inorganic Process Industries, Macmillan Company, p. 185 (1948).

235. Kopita, R. and Gleason, T. G., "Wet Scrubbing of Boiler Flue Gas," Chem. Eng. Progr. 64 (1), 74-80 (1968).

236. Koval, E. J. and Peters, M. S., "How Does Nitric Oxide Affect Reactions of Aqueous Nitrogen Dioxide?" Ind. Eng. Chem. 52, 1011-14, (1960).

237. Kurin, I. N. P. and Blokh, I. O., "Catalytic Oxidation of Nitric Oxide," J. Applied Chem. (U.S.S.R.) 11, 734-49, (1938).

238. Kuz'minykh, I. N., Aigina, E. P. and Babushkina, M. D., "Absorption of Nitrogen Oxides by Soda and Lime Solutions," Khim. Prom. 1953, No. 8, 26-7.

239. Kuz'minykh, I. N., Rodionov, A. I. and Mishchenko, Y. S., "Absorption of Nitric Oxide from Nitrogenous Exhaust Gases in Large-Scale Plate Columns," Tr. Mosk. Khim.-Tekhnol. Inst. 1961, No. 33, 43-7.

240. Levenson, D. A., "Recovery of Oxides of Nitrogen by Absorption," Yale University, 1945.

BIBLIOGRAPHY (PRELIMINARY 1/69)

241. Linde, German Patent 521,031 (1929). "Removing Nitric Oxide from Gases."

242. Lindsay, W. N., et al, "Methods and Apparatus for the Recovery of Nitrogen Oxides from Gaseous Mixtures," U.S. Patent #2,674,338, April, 1954.

243. Lovejoy, D. L., et al, "Dinitrogen Trioxide. Part VI. The Reactions of Dinitrogen Trioxide with Primary and Secondary Amines," J. Chem. Soc. A. 1968, 2325-8.

244. Lozhkin, A. F. and Subochev, N. L., "Recovery of Nitrogen Oxides from Lean Gases by Activated Carbon in a Moving Bed," Sb. Nauch. Tr., Perm. Politchk. Inst. No. 18, 61-74 (1965).

245. Lucas, D. H., James, K. W. and Davies, I., "Measurement of Plume Rise and Dispersion at Tilbury Power Station," Atoms. Environ. 1(4), 353-65 (1967).

246. Malin, K. M., "Sulfuric Acid Technology," Russian State Chem. Press (1950).

247. Manchot, W., Konig, J. and Reinlinger, S., "A Compound of Sulfur Trioxide and Nitric Oxide, and the Theory of the Lead Chamber Process," Ber. 59B, 2072-81 (1926).

248. Manchot, W. and Schmid, H., "Metallic Nitroso Compounds: A Nitric Oxide Compound of Manganese," Ber. 59, 2360-3 (1926).

249. Manchot, W. and Schmid, H., "The Reaction of Sulfur Dioxide with Nitrogen Dioxide," Ber. 62B, 1261-3 (1929).

250. Manvelyan, M. G., Grigoryan, G. O. and Gazaryan, S. A., "The Joint Recovery of Low Concentrations of Sulfur Dioxide and Nitrogen Oxides by Alkaline Solutions and Carbonates. I.," Izvest. Akad. Nauk. Armyan. S.S.R., Khim. Nauki 12, 165-74 (1959).

251 Manvelyan, M. G., Grigoryan, G. O., Gazaryan, S. A., Papyan, G. S. and Mirumyan, R. L., "Simultaneous Absorption of Small Amounts of Sulfurous and Nitrous Gases by Alkalis and Carbonates. III. Preparation of Gypsum in a Large-Scale Laboratory Unit," Izvest. Akad. Nauk Armyan. S.S.R., Khim. Nauki 12, 313-23 (1959).

252. Manvelyan, M. G., Grigoryan, G. O., Gazaryan, S. A., Papyan, G. S., Karakhanyan, S. S. and Malik-Israelyan, L. S., "Simultaneous Absorption of Low Concentrations of Sulfur Dioxide and Nitrogen Oxides by Alkalies and Carbonates. VI. Effect of Inhibitors on Oxidation of Calcium Sulfite to Calcium Sulfate by Air in the Presence of Traces of Nitrogen Oxides," Izvest. Akad. Nauk Armyan. S.S.R., Khim. Nauki 14, No. 1, 27-33 (1961).

BIBLIOGRAPHY (PRELIMINARY 1/69)

253. Markvart, M. and Pour, Vl., "The Influence of Oxygen on the Catalytic Reduction of Nitric Oxide by Ammonia," J. Catal. 7(3), 279-81 (1967).

254. Marsh, K. J. and Foster, M. D., "An Experimental Study of the Dispersion of the Emissions from Chimneys in Reading. I. The Study of Long-Term Average Concentrations of Sulfur Dioxide, II. A Description of the Instruments Used," Atmos. Environ. 1 (5), 527-59 (1967).

255. Martin, A. and Barber, F. R., "Investigations of SO_2 Pollution Around a Modern Power Station," J. Inst. Fuel (London) 39, (306), 294-307 (July 1966).

256. Martin, A. and Barber, F. R., "Sulphur Dioxide Concentrations Measured at Various Distances Form Modern Power Station," Atmos. Environ. 1(6), 655-77 (Nov. 1967).

257. Maury, et al, "Methods of Removing Nitrogen Oxides and Nitrous Acid from Fluids," U.S. Patent #3,044,844 (1962).

258. Mellor, "Other Reactions of Nitric Oxides," Treatise on Inorganic & Theoretical Chem., Vol. VIII, Supplement II, Part II, (1967).

259. Michailova, E. A., "The Kinetics of the Reaction Between Ammonia and Nitric Oxide on the Surface of a Pt Filament," Acta Physicochimica U.R.S.S. X, No. 5, 653-676 (1939).

260. Mirev, D., Balarev, Khr., Boyadzhiev, L. and Lambiev, D., "Absorption of Nitrogen Oxides by Vibrating Layers of NaOH Solutions," Compt. Rend. Acad. Bulgare Sci. 14, 250-62 (1961).

261. Moeller, T., Inorganic Chemistry, John Wiley & Sons, p. 598 (1952).

262. Montgomery, T. L. and Corn, M., "Adherence of Sulfur Dioxide Concentrations in the Vicinity of a Steam Plant to Plume Dispersion Models," J. Air Pollut. Contr. Assoc. 17(8), 512-17 (1967).

263. Moore, D. J., "SO_2 Concentration Measurements Near Tilbury Power Station," Atmos. Environ. 1(4), 389-410 (1967).

264. Morecroft, M. J. and Thomas, J. H., "The Reaction Between Nitric Oxide and Oxygen," J. Phys. Chem. 71(5), 1543-4 (1967).

265. Morrison, M. E., Rinker, R. G., and Corcoran, W. H., "Rate and Mechanism of Gas-Phase Oxidation of Parts-Per-Million Concentrations of Nitric Oxide," Indus.& Eng. Chem. - Fundamentals v 5 n 2, May 1966, 175-81.

266. Mucskai, L., "The Oxidation of Nitrogen Oxides During Continuous Equimolecular NO + NO_2 Absorption from Dilute Waste Gases," Magyar Kem. Folyoirat 67, 488-90 (1961).

BIBLIOGRAPHY (PRELIMINARY 1/69)

267. Muller, Von E., et al, "Uber die Zersitzung Von Stickoxyd beim Erhitzen mit Metallen," Zeit. fur Anorg. und Allg. Chem. 129, 309-320 (1923).

268. Nabiev, M. K., Kulik, A. A., Merenkov, P. T. and Tikhonenko, A. D., "Recovery of Nitrogen from Dilute Nitric Acid Waste Gases for Ammonia Synthesis," Dokl. Akad. Nauk Uz. SSR 20(11), 17-20 (1963).

269. Neumann, B. and Rose, G., Z. Angew. Chem. 33, 41 (1920).

270. Nobe, K. and Wikstrom, L. L., "Catalytic Decomposition of Nitrogen Dioxide," Am. Chem. Soc., Div. Water Waste Chem., Preprints 1963 (March-April), 268-73.

271. Nonnenmacher, H., et al, U.S. Patent #3,279,884, "Selective Removal of Oxides of Nitrogen from Gas Mixtures Containing Oxygen," Filed U.S. Patent Office, September 21, 1964.

272. Nyholm, S. and Rannitt, L., "N-Nitrosohydroxylamine-N-Sulfonates, Procedure A."

273. Palka, J., "The Danger of NO in Producer Gas and Methods for Its Removal," Chem. Prumsyl (Prague) 17(6), 327-329 (1967).

274. Pauling, H., "Complete Removal of Nitrogen Oxides," Neth. Appl. 6,606,577, Nov. 21, 1966; Ger. Appl. May 18, 1965; 14 pp.

275. Pawlikowski, S., Stanislaw, A. and Bristron, S., "Experiments of NH_3 Absorption of N Oxides in the Nozzle Systems on Semitechnical Scale. II. Absorption by a Mixture of Ammonium Carbonate and Bicarbonate Solutions," Przemysl Chem. 43(2), 80-3 (1964).

276. Perov, E. V., "Absorption of Nitrogen Oxides by Magnesium, Strontium, and Barium Hydroxides," Tr. Novocherk. Politekhn. Inst. 121, 57-60 (1961).

277. Peters, G. H., "A Solid Chemical Air Generator (Decomposition of NO_2)," Biomedical Lab., Aerospace Medical Res. Labs., Amoco Chemicals Corp.

278. Peters, M. S., et al, "Controlling Mechanism in the Aqueous Absorption of Nitrogen Oxides," A.I.Ch.E. Journal, 1, 105-11, 1955.

279. Peters, M. S., "Stop Pollution by Nitrogen Oxides," Chem. Eng. 62, 197-200, May 1955.

280. Peters, M. S., et al, "Vapor - and Liquid - Phase Reactions Between NO_2 and H_2O," Ind. Eng. Chem., Vol. 47, 2536-9, 1935.

281. Pierce, J. A., "A Study of the Reaction Between Nitric Oxide and Hydrogen Sulphide," J. Am. Chem. Soc. 47, 2173 (1925), J. Phys. Chem., 1929, 33, 22-36.

282. Pike, R. D., U.S. Patent #2,800,392, "Nitric Oxide," July 23, 1967.

BIBLIOGRAPHY (PRELIMINARY 1/69)

283. Pike, R. D., U.S. Patent #2,647,822, "Nitric Oxide Recovery," August 4, 1953.

284. Plumley, A. L., Jonakin, J., Whiddon, O. D. and Shutko, F. W., "Removal of Sulfur Dioxide and Dust from Stack Gases," Proc. Amer. Power Conf. 29, 592-614 (1967).

285. Pollock, W. A., et al, "Removal of Sulfur Dioxide and Fly Ash from Coal Burning Power Plant Flue Gases," ASME Publication 66-WA/CD-4.

286. Pound, J. R., "The Oxidation of Solutions of Ferrous Salts," J. Phys. Chem. 43, 955 (1939).

287. Pozin, M. E., Kopylev, B. A. and Bel'chenko, G. V., "The Abosrption of Nitrogen Oxides in Soda Solutions in the Penn Apparatus for the Production of Sodium Nitrate," Trudy Leningrad. Teknol. Inst. im. Lensoveta 36, 120-32 (1956).

288. Pozin, M. E., Zubov, V. V., Tereshchenko, L. Ya., Tarat, E. Ya. and Ponomarev, Yu. L., "Solubility of NO in Aqueous Solutions of Various Salts," Izv. Vysshikh Uchebn. Zavedenii, Khim. i. Khim. Tekhnol. 6(4), 608-16 (1963).

289. "Process Wrings Pure N from Nitric Fumes," Chem. Eng. (Oct. 16, 1961), pp. 102 and 104.

290. Purtseladse, K. H., et al, "Absorption of Nitrogen Oxides by Manganese Hydroxide," Trudi Inst. Metalla I. Gornogo Dela AH Grusinskoi SSR V, VII 1956.

291. Rabson, S. R., "Development of an Extraction Plant for the Elimination of Blasting Fumes," Trans. Commonwealth Mining Met. Congr. 2, 757-74 (1961).

292. Rabson, S. K., "Vermiculite in the Absorption of Gases, Vapors, and Fumes," Industrial Chemist 37, 219-20 (1961).

293. Rao, M. N., et al, "Catalytic Oxidation of NO on Activated Carbon," Chem. Eng. Prog. Symp. Series, #4, Vol. 48, 110-124 (1952).

294. Reese, J. T., et al, "Electro Static Precipitation," Mechanical Engineering, October 1968.

295. Reinders and Cats, Chem. Weekblatt 9, 47 192.

296. Reitmeier, R. E., U.S. Patent #2,924,504, "Process of Removing Nitrogen Oxides from Gas Streams of Varying Composition," Filed August 30, 1956, Patented February 6, 1960.

BIBLIOGRAPHY (PRELIMINARY 1/69)

297. Riese, V. W., et al., "Uber die Brauchbarkeit von Aktivkoks fur die Entfernung geringer Gehalte von Oxyden des Stickstoffs aus Gasen," Brennstoff - Chemie 21, Feb. 1940, pp. 25-36.

298. Riesz, C. H., Morritz, F. L. and Franson, K. D., "Catalytic Decomposition of Nitric Oxide," Air Pollution Foundation Rept., No. 20, 22 pp. (1957).

299. Robins, D. L and Mattia, M. M., "Computer Program Helps Design Stacks for Curbing Air Pollution," Chem. Eng. v 75 n 3, (Jan. 29, 1968), pp. 119-22.

300. Rodionov, A. I., Mishchenko, Yu. S., Klimov, A. P. and Bogdanov, E. A., "Absorption of Nitrogen Oxides with a Suspension of Limestone," Tr. Mosk. Khim. Tekhnol. Inst. (40), 74-7 (1963).

301. Rose, A. H., Jr., Stenburg, R. L., Corn, M., Horsley, R. R., Allen, D. R. and Kolp, P. W., "Air Pollution Effects of Incinerator Firing Particles and Combustion Air Distribution," J. Air Pollution Control Assoc. 8, 297-309 (1959).

302. Roth, J. F. and Doerr, R. C., "Air Pollution Studies: Oxidation-Reduction Catalysis," Ind. Eng. Chem. 53, 293-6 (1961).

303. Ryason, P. R., "Studies on New Method of Simultaneously Removing SO_2 and NO_x from Comb. Gases," APCA, Vol. 17 n 12, December 1967, 796-9.

304. Saenz, O., McKee, H. C., Hiser, L. L. and Reinauer, T. V. "Simultaneous Removal of Sulfur Dioxide and Oxides of Nitrogen from Flue Gases," APCA 68-181, June.

305. Safiullin, N. Sh. and Tseitlin, A. N., "Absorption of Nitrogen Oxides by Sulfuric Acid," Zh. Prikl. Khim. 36, 490-5 (1963).

306. Safiullin, N. Sh. and Olevinskil, M. I., "Rendering Harmless the Tail Gases from Sulfuric Acid Chamber Process," Khim. Prom. 132-6 (1955).

307. Sakaida, R. R., Rinker, R. G., Wang, Y. L. and Corcoran, W. H., "Catalytic Decomposition of Nitric Oxide," A.I.Ch.E. J. 7, (4), 658-63 (1961).

308. Sartori, G. and Ercolani, C., "The Absorption of NO on Solid Fe(II)-Phthalocyanine," Ric. Sci., Rend. Sez. A 3(3), 323-8 (1963).

309. Saunders, E. and Ressmann, E., "Study of the Feasibility of Oxidizing the SO_2 in Power Plant Flue Gas to Sulfuric Acid," Tyco Laboratories, Inc. First Interim Progress Report under NAPCA Contract PH 86-68-75, Jan. 1-July 31, 1968.

BIBLIOGRAPHY (PRELIMINARY 1/69)

310. Schmidt, A. and Weinrotter, F., "Separation of NO and NO_2," Ger. 1,075,571 (Feb. 18, 1960).

311. Schmidt, K. H. and Schulze, V., "Removal of Nitrogen Oxides from Gases by Catalytic Reduction to Nitrogen," Ger. 1,259,298 (Jan. 25, 1968, Appl. Aug. 20, 1964).

312. Schutze, Von, Dr. M., "Feinreinigung von Gasen mit einem Hochaktiven Kupferkatalysator," Angew Chem. 70, 697-699 (Nov. 22-23, 1958).

313. Schwab, G. M. et al., "The Effect of Metallic Oxides in Decomposing Nitric Oxide and Their Place in the Periodic Table,"

314. Scorer, R. S. and Barrett, C. F., "Gaseous Pollution from Chimneys," Int. J. Air & Water Pollution (Jan-Feb., 1962).

315. Sebastiani, E., "Elimination of Nitrogen Oxides," Securitas (Rome) 51(5), 31-44 (May, 1966).

316. Shah, H. S., "The Combustion of Charcoal in O_2, NO and N_2O. Part II: The Effect of Temperature," J. Chem. Soc. (1929), pp. 2676 and 2692.

317. Shelef, M. and Otto, K., "Appearance of Nitrous Oxide in the Catalytic Reduction of Nitric Oxide by Carbon Monoxide," J. Catal. 1968, 10 (4), 408-12.

318. Shelef, M., "Catalytic Reduction of Nitric Oxide. First National Symposium on Heterogeneous Catalysis for Control of Air Pollution, Franklin Institute, Phil., Pa., Nov. 1968.

319. Sherwood, T. K. and Pigford, R. L., "Absorption and Extraction," Chemical Eng. Series, McGraw-Hill.

320. Shively, W. L., "Electrical Removal of Gum-Forming Constituents from Manufactured Gas," Trans. of the Electrochemical Soc. 69 (1936), pp. 495-517.

321. Siek, U. H., "The Preparation of Nitrogen from the Tail Gas of Nitric Acid Plant," K'o Hsueh T'ung Pao 10, 307-8 (1957).

322. Sihnenemen, J. J., "Iron and Steel Making Process-Flow Sheets and Air Pollution Controls," American Conf. of Governmental Industrial Hygienists (1961).

323. Simons, W., "Measuring Emissions Occurring at Small-Sized Refuse Incineration Facilities," Tech. Ueberwach. 7(12), 413-15 (1966).

BIBLIOGRAPHY (PRELIMINARY 1/69)

324. Slack, A. V., "Air Pollution: The Control of SO_2 from Power Stacks Part III - Processes for Recovering SO_2," Chemical Engineering, p. 188 Dec. 1967.

325. Smith, R. N., Lesnini D. and Mooi, J., "The Anomalous Adsorptive Properties of Nitric Oxide," J. Phys. Chem. 60, 1063-6 (1956).

326. Smith, M. E., "Reduction of Ambient Air Concentrations of Pollutants by Dispersion from High Stacks," Combustion 38(10), 23-7 (1967).

327. Smyslov, N. I., "Means for Removing Toxic Wastes of the Sulfuric Acid Tower Process," Ochistka i Ispol'z. Stochn. Vod i Prom. Vybrosov, Kiev, Sb. 88-93 (Russ) (1964).

328. Sourirajan, S. and Blumenthal, J. L., "Catalytic Decomposition of Nitric Oxide Present in Low Concentrations," Proc. Intern. Congr. on Catalysis, 2nd, Paris, 1960, 2, 2521-38.

329. Stanislav, J., Josef, K. and Jiri, S. "Utilization of Bound Nitrogen in Catalytic Reduction of Nitrogen Oxides," Czech. 124,669 (Oct. 15, 1967, Appl. Nov. 6, 1963).

330. Stenburg, R. L., Horsley, R. R., Herrick, R. A. and Rose, A. H., Jr., "Effects of Design and Fuel Moisture on Incinerator Effluents," J. Air Pollution Control Assocn. 10, 114-20 (1960).

331. Stenburg, R. L., Hangebrauck, R. P., Von Lehmden, Darryl, J. and Rose, A. H., Jr., "Field Evaluation of Combustion Air Effects on Atmospheric Emissions from Municipal Incinerators," APCA Journal 12 No. 2 (83-89).

332. Stephens, E. R., "The Role of Oxygen Atoms in the Atmospheric Reaction of Olefins with Nitric Oxide," Air and Wat. Pollut. Int. J. 10, 793-803 (1966).

333. Stoddart, E. M., "Reaction of Phosphoric Anhydride with Nitrogen Dioxide and with Nitric Oxide," J. Chem. Soc., 1938, 1459-61.

334. Stone, G. N. and Clarke, A. J., "British Experience with Tall Stacks for Air Pollution Control on Large Fossil-Fueled Power Plants," Proc. Amer. Power Conf. 29, 540-56 (1967).

335. Stopperka, K. and Wolf, F. "Gas-Phase Reaction of Nitrogen Dioxide and Sulfur Dioxide," Z. Anorg. Allg. Chem. 359(1-2), 14-29 (1968).

336. Straschill, M., "Disposal of Nitrogen Oxide Containing Waste Gases in Pickling Plants," Metall-Reinigung Vorbehand. 12(11), 210-11 (1963).

337. Strauss, W., "Industrial Gas Cleaning," Pergamon Press (1966).

BIBLIOGRAPHY (PRELIMINARY 1/69)

338. Streight, H. R. L., "Reduction of Oxides of Nitrogen in Vent Gases," Can. J. Chem. Eng. 36, 3-11 (1958).

339. Strelzoff, S., "Today's Routes to Nitrophosphate Fertilizers," CE 121-126 (July 15, 1968).

340. Sundaresan, B. B., Harding, C. I., May, P. P. and Hendrickson, E. R., "Adsorption of Nitrogen Oxides from Waste Gas," Environ. Sci. Technol. 1, (2) 151-6 (1967).

341. Sundaresan, B. B. and Harding, C. I., U.S. Patent #3,389,961, "Methods of Recovering Gases and Vapors," June 25, 1968, Appl. 14, January 1966, 5 pp.

342. Taylor, F. R., "Elimination of Oxides of Nitrogen from Automobile Exhaust," Air Pollution Foundation Report (LA) #28 (1959).

343. Toro, R. F. and Weinstein, J., "Air Pollution Control Needs Spur Catalyst Sales," Environmental Science and Technology, 3 (1), 30 (Jan. 1969).

344. Tow, P. S., "The Feasibility of Control of Oxides of Nitrogen," J. Air Pollution Control Assoc. 7, 234-40 (1957).

345. Treacy, J. C. and Daniels, F., "Kinetic Study of the Oxidation of Nitric Oxide with Oxygen in the Pressure Range 1 to 26 mm," J. Am. Chem. Soc. 77, 2033-6 (1955).

346. Trofimov, A. I., "Purification of Coke-Oven Gas from Nitrogen Oxides," Koks i Khim. (2), 42-3 (1966).

347. Tseitlin, A. N. and Romanenko, K. E., "Nitrogen Oxide Absorption by Sulfuric Acid," Izv. Vysshikh Uchebn. Zavedenii, Khim. i. Khim. Tekhnol. 9(1), 85-8 (1966).

348. Tsutsumi, H., "Treatment of Nitrogen Oxides in Waste Gases," Ryusan 20(9), 193-5 (1967) (Japan).

349. Tuerkoelmez, S., "Synthetic Resin Ion Exchanger for Eliminating Obnoxious Odors Through Exchange Adsorption," Wasser Luft Betrieb 9(11), 737-43; (12), 812-16 (1965) (Ger).

350. Turner, D. B., Commentary on "Full-Scale Study of Dispersion of Stack Gases," U.S. DHEW, PHS, Div. Air Pollution, Cincinnati, Ohio (Dec., 1965).

351. Tyler, B. J., "Reaction of Hydrogen Peroxide and Nitric Oxide," Nature 195, 279-80 (1962).

BIBLIOGRAPHY (PRELIMINARY 1/69)

352. Vaillant, G., "Fight Against Atmospheric Pollution in the Fertilizer Industry," Inform. Chim. No. 43, 69, 63-6 (1966).

353. Varlamov, I. M., Manakin, G. A., Starosel'skii, Ya. I. and Zbrozhek, L. S., "Ammonia Method for Removing Nitrogen Oxides from Exhaust Gases of a Tower Nitrose Sulfuric Acid System," Nauchn. Zap. Odessk. Politekhn. Inst. 40, 24-33 (1962).

354. Veal, D. J., U.S. Patent #3,050,363, "Removal of Nitric Oxide from Gas Streams," Filed July 28, 1958.

355. Vetter, K., "Kinetics of the Thermal Decomposition and Formation of Nitric Oxide," Z. Elecktrochem. 53, 369 (1949).

356. Visvanathan, K. S., "The Decomposition of Nitric Oxide in the Silent Electric Discharge," J. Indian Chem. Soc. 29, 307-16 (1952).

357. Vogel, H., "Elimination of Nitrogen Oxides in Waste Gases," Chemiker Ztg. 89(18), 632-5 (1965) (Ger).

358. Von Schuftan, P., "Uber schwere Kohlenwasserstoffe und Andere Bestandteile des Koksofengases von den Kohlen and den Mineralolen," Berlin, Verlag Chemie I, 205; II, 31 (1928 and 1929).

359. Wahl, M. H., U.S. Patent #2,382,189, "Preparation of Nitric Oxide," Filed July 20, 1940.

360. Walker, A. B., et al., "Characteristics of Furnace Emissions from Large Mechanically Stoked Municipal Incinerators," National Incinerator Conference, ASME, New York City (May, 1966).

361. Wikstrom, L. L. and Nobe, K., "Catalytic Dissociation of Nitrogen Dioxide," Ind. Eng. Chem., Process Design Develop. 4, (2), 191-5, (1965).

362. Yost, D. M. and Russel, H., Systemic Inorganic Chemistry, Prentice Hall, p. 30 (1946).

363. Yuan, E. L., Slaughter, J. I., Koerner, W. E. and Daniels, F., "Kinetics of the Decomposition of Nitric Oxide in the Range 700-1800°," J. Phys. Chem. 63, 952-6 (1959).

364. Private communication from E.I. DuPont de Nemours & Co., Wilmington, Del.

365. Private communication from Engelhard Industries, Newark, N.J.

366. Private communication from Kyowa Chemicals, Ltd., Ube, Japan.

367. Private communication from Princeton Chemical Research, Princeton, N.J.

368. Private communication from Southern California Edison, Los Angeles, Calif.

369. Private communication from Battelle Memorial Institute, Walling, F.J., Columbus, Ohio.

370. Private communication from Esso Research and Engineering Co., unpublished data.

BIBLIOGRAPHY (PRELIMINARY 1/69)

Combustion Modifications

400. "Advances in Energy Conversion Engineering," papers presented at the 1967 Intersociety Energy Conversion Engineering Conference, ASME, Miami Beach (August, 1967).

401. Advisory Committee Report, No. 7 on "Conventional Steam-Electric Generating Stations," prepared by a Subcommittee of the Generating Stations Special Committee (April, 1963).

402. Air Pollution Engineering Manual, PHSP #999-AP-40.(Duplicate 696)

403. Alperstein, M. M. and Bradow, R. L., "Exhaust Gas Emissions Related to Engine Combustion," SAE J. 75(7), 52-3 (July, 1967).

404. Anastassakis, K., "Composition of Diesel Exhaust Gases," Chim. Chronika 31(7), 81-7 (1966) (Greek).

405. Andrews, R. L., "Effect of Flue Gas Recirculation on Emissions from Heating Oil Combustion," APCA Paper #68-21.

406. Austin, H. C. and Chadwick, W. L., "Control of Air Pollution from Oil-Burning Power Plants," Mech. Eng. 82(4), 63-6 (April, 1960).

407. Barnhart, D. H. and Diehl, E. K., "Control of Nitrogen Oxides in Boiler Flue Gases by Two-Stage Combustion," J. Air Pollution Control Assoc. 10, 397-406 (1960).

408. Barry, P. J., "Frequency of Occurrences of Maximum Pollution Levels from Single Stacks," AEC Accession No. 33503, Rept. No. AECL-2575 8 pp. (1966) (Eng).

409. Benforado, D. M., Pauletta, C. E. and Hazzard, N. D., "Economics of Heat Recovery in Direct Flame Fume Incineration," Air Eng. 9(3), 29-32 (1967) (eng).

410. Brubacher, M. L., "Formation and Control of NO_x in Gasoline Engines," presented at 5th AIChE Southern California Section Annual Technical Meeting, Los Angeles (May 25, 1968).

411. Brunner, M., "The Composition of the Exhaust Gases from Gasoline Engines," Z. Praeventivmed 11, 77-103 (1966).

412. Cejka, M., "Exhaust Gases from Compression Ignition Engines," Ropa Uhlie 9(6-7), 208-11 (1967) (Czech).

BIBLIOGRAPHY (PRELIMINARY 1/69)

413. Chaikivsky, M., "Nearly Stoichiometric Combustion of Heavy Fuel Oils," Erdoel Kohle, Erdgas, Petrochem. 21(2), 86-90 (1968) (Ger).

414. Cooper, P. W., "Recirculation and Fuel-Air Mixing as Related to Oil-Burner Design," API Publication 1723 (May, 1964).

415. Crouse, L. F., "A Pollution Solution by Direct Gas-Fired Industrial Fume Incineration," Liquid & Gaseous Waste Incineration Symposium, May 1968.

416. Darby, K, et al., "Konditionierung der Rauchgase von Kesselanlagen Zur Verbesserung des Abscheidegrades von Elektrofiltern," Staub-Reinhaltung der Luft 26(11), 464-8 (November, 1966).

417. DeCorso, S. M., Hussey, C. E. and Ambrose, M. J., "Smokeless Combustion in Oil-Burning Gas Turbines," ASME Paper 67-PWR-5 for meeting 8 p. (Sept. 24-28, 1967).

418. Delyagin, G. N., et al., "Analysis of Heat Losses from Flue Gases during the Combustion of a Water-Coal Suspension," Szhiganic Vysokoobvodn, Topl. Vide Vodougol. Suspenzii 166-74 (1967).

419. Durrant, T., "The Control of Atmospheric Pollution from (Aircraft) Gas Turbine Engines," SAE Air Transp. Mtg., New York (April 29 - May 2, 1968).

420. Eyzat, P. and Guibet, J. C., "A New Look at Nitrogen Oxides Formation in Internal Combustion Engines," SAE Paper 680124 for meeting, 18p. (Jan. 8-12, 1968).

421. Eyzat, P. and Guibet, J. C., "Etude de I'inflammation dans les Moteurs Diesel," Inst. Francais du Petrole et Annales des Combustibles Liquides--Rev. 22(12), 1856-74 (Dec. 1967).

422. Fernandes, J. H., "Boiler Emissions and Their Control," presented at Conference on A.P. Control, Mexico City, Mexico (April 28, 1966).

423. Field, M. A., et al., "Combustion of Pulverized Coal," (book), The British Coal Utilization Research Assoc. (1967).

424. Frankel, R. J. "Oxides of Nitrogen from Utility Boilers - A Critique of Current Knowledge," Resources for the Future, Inc., Washington, D. C. (unpublished paper).

425. Frey, D. J., "Deashed Coal Combustion Study," prepared for OCR by contract with Combustion Engineering, Inc., (Period May-December, 1964).

BIBLIOGRAPHY (PRELIMINARY 1/69)

426. Gartrell, F. E., "Control of Air Pollution from Large Thermal Power Stations," Rev. Soc. Roy. Belge Ing. Ind. No. 11, 471-82 (1966) (Eng).

427. George, R. E. and Chass, R. L., "Control of Contaminant Emissions from Fossil Fuel-Fired Boilers," Amer. Chem. Soc., Div. Fuel Chem., Preprints 10(1), 31-55 (1966) (Eng).

428. Grieswold, S. S., Chass, R. L., George, R. E. and Holmes, R. G., "Evaluation of Natural Gas in Reducing Industrial Air Pollution," Gas Age 128(2), 36-9 (July 20, 1961).

429. Gross, G. P. "Control of NO in Automotive Exhaust," private communication.

430. Gross-Gronomski, L., Wacholder, E., Rotstein, D. and Kabin, D., "Influence of Intake Air Temperature on Smoke Emission in Diesel Engine," Inst. Fuel 40(319), 352-7 (August, 1967).

431. Haese, U., "Heutige Messtechnik und neuere Ergebnisse der Internationalen Flammenforschung," Zement-Kalk-Gips 20(6), 257-66 (June, 1967).

432. Haupt, C. G., "Exhaust Emission by a Small Gas Turbine," SAE Midyear meeting, Detroit, Paper No. 680463 (May 20-24, 1968).

433. Harkins, J. and Goodwine, J. K., "Oxides of N in Diesel Exhaust," J. Air Pollution Control Assoc. 14(1), 34-8 (1964).

434. Herbst, W. A., "The Automotive Gas Turbine--Its Fuel and Lubricant Requirements," SAE Metropolitan Section, Paper No. 660341 (March 10)

435. Herbst, W. A., "Fuel Behavior in a Regenerative Gas Turbine Engine," SAE National Transportation, Powerplant and Fuels and Lubricants Meeting, Paper No. 938A, Baltimore (October, 1964).

436. Herbst, W. A. and Hakala, N. V., "Stationary Applications of Gas Turbines and Their Fuel Requirements," Proceedings of the Seventh World Petroleum Congress, Mexico City, p. 67 (1967).

437. Hoffman, H., "The Composition of Exhaust Gases from Diesel Motors," Z. Praeventivmed. 11, 104-21 (1966).

438. Hoffmann, H., "Exhaust Gas Problems with Gasoline and Diesel Motors. I. Gasoline Engines," Erdöl Kohle 20(8), 564-8 (August, 1967)

439. Hoffmann,H., "Exhaust Gas Problems with Gasoline and Diesel Engines. II. Diesel Engines," Erdöl Kohle 20(9), 644-8 (September, 1967).

BIBLIOGRAPHY (PRELIMINARY 1/69)

440. Holl, R., "Results of A.P. Measurement Programs in the Vicinity of Thermal Plants of the French Electricity Co.," (EDF) 37(1), 17-38 (1968).

441. Huebler, J., "Coal Hydrogasification," Chem. Eng. Prog. 42(2), 87-91 (February, 1966).

442. Kopa, R. D., et al., "Exhaust Gas Recirculation as a Method of NO_x Control in an Internal-Combustion Engine," 53rd Annual Meeting, APCA, Cincinnati, (May, 1960).

443. Kukin, I., "Chemical Supplements for Diesel Air Pollution Control Programs," ASME--Paper 68-DGP-14 for meeting, 5 p. (May 12-16, 1968).

444. Lenz, H. P., "Fuel Injection Using Nonstationary Hydrodynamics," Motortech. Z. 28(S), 301-7 (August, 1967).

445. Linnell, R. H. and Scott, W. E., "Diesel Exhaust Composition and Odor Studies," J. Air Pollution Control Assoc. 12(545), 510-15 (1962).

446. Lozano, E. R., Melvin, W. W., Jr. and Hochheiser, S., "Air Pollution Emissions from Jet Engines," J. Air Pollution Control Association 18(6), 392-94 (June, 1968).

447. Mache, A. and Authier, R., "Transformation au Mazout des Generateurs de Vapeur de la Centrale Arrighi," Genie Civil 142(5), 82-104 (March 1, 1965).

448. Merrion, D. E., "Science/Technology: Effect of Design Revisions on Two Stroke Cycle Diesel Engine Exhaust," SAE Mid-year meeting, Detroit, Paper No. 680422 (May 20-24, 1968).

449. Monroe, E. S., et al., "Low Excess Air Operation of Furnaces," presented before the Joint Technical Conference on Clean Air, APCA, Trenton, N.J. (November, 1964).

450. Muller, Von, E., et al., "Uber die Zersetzung Von Stickoxyd beim Erhitzen mit Metallen," Zeit fur Anorg und Allg Chem. Bd. 129, pp. 309-320 (Duplicate 285).

451. Newhall, H. K. and Starkman, E. S., "Ammonia Versus Hydrocarbons as Gas Turbine Fuels," SAE (Soc. Automot. Eng.) J. 75(6), 71-7 (1967).

452. Novobilski, J. A., "Low Excess Oxygen Firing (and the Use of Low Excess Fuel Oil) in Large Central Station Boilers (to Reduce Air Pollution)," Presented at 5th AIChE Southern California Section, Annual Technical Meeting, Los Angeles (April 25, 1968).

BIBLIOGRAPHY (PRELIMINARY 1/69)

453. Ourusoff, L., "Air Pollution," Am. Gas J. 194, No. 3, 32-5, 38, 40, 42 (Mar. 1967).

454. Paleari, C. and Rennanigo, F., "Combustion Products of Diesel Fuels. I. Effect of Ignition Promoters on Formation of CO and Nitrogen Oxides," Riv. Combustibil 13, 419-31 (1959).

455. Pegg, R. E. and Ramsden, A. W., "Towards Cleaner Diesel Engine Exhausts," Int. Clean Air Congr., Proc., London, Pt. 1, 154-6 (1966).

456. Rohrman, F. A., Ludwig, J. H. and Steigerwald, B. J., "Coal Utilization and Atmospheric Pollution," Coal Today & Tomorrow 19, No. 4, 5-7 (Apr. 1965).

457. Shibuya, Toshikazu, "Engine Performance Seen From the Exhaust Smoke Density of Single Cylinder Diesel Engine. II. Effect of Air-Fuel Ratio and Products of Combustion on the Exhaust Smoke Density," Shigakenritsu Tanki Daigaku Gakujutsu Zasshi No. 8, 1-5 (1967).

458. Singer, Joseph M., Cook, E. B., Harris, Margaret E., Rowe, Valeria R. and Grumer, Joseph, "Flame Characteristics Causing Air Pollution. Production of Nitrogen Oxides and Carbon Monoxide," U.S. Bureau Mines, Rep. Invest. No. 6958, 34 pp. (1967).

459. "Smogless Stirling Engine Promises New Versatility," Product Engng. 39, 30-33 (Feb. 26, 1968).

460. Spindt, R. S., Wolfe, Court L. and Stevens, Donald R., "Nitrogen Oxides, Combustion and Engine Deposits," J. Air Pollution Control Assoc. 6, 127-33 (1956).

461. Squires, A. M., "Clean-Fuel Power Cycles," Paper 67-WA/PWR-3.

462. Stephens, E. R., Hanst, P. L., Doerr, R. C. and Scott, W. E., "Auto Exhaust: Composition and Photolysis Products," J. Air Pollution Control Assoc. 8, 333-5 (1959).

463. Styles, H. E. "Public Health Aspects of Air Pollution from Diesel Vehicles," World Health Organization WHO/AP/67.28.

464. Taylor, W. G., "Reducing Smoke from Gas Turbines," Mech. Eng. 90(7), 29-35 (July, 1968).

465. Tersilla, D. O. di Borgatti, "Removal of Nitric Oxides from the Ozonized Air Emitted by Ozonizers," 2 pp., (December 10, 1962).

466. Tomaras, Z. G. and Reckner, L., "Tests of an Air Atomizer Burner-Boiler Unit Using No. 6 Oil," U. S, Public Health Service (February, 1968). "Tests of a Rotary-Cup Burner-Boiler Unit Using No. 6 Oil."

BIBLIOGRAPHY (PRELIMINARY 1/69)

467. Tomaras, Z. G. and Reckner, L., "Tests of a Steam Atomized Burner-Boiler Unit Using No. 6 Oil," U. S. Public Health Service (March, 1968).

468. Turner, J. S., "Intermittent Release of Smoke from Chimneys," J. Mech. Eng. Science 2, No. 2, 97-108 (June 1960).

469. Varshavskii, I. L., Zolotarevskii, L. S. and Frenkel, A. O., "Separation of Oxides of Nitrogen in Engines with External Carburetion, Using Gas Fuel," Gas Prom. 11(7), 36-9 (1966).

470. Waid, D. E., "Incineration of Organic Materials by Direct Gas Flame for Air Pollution Control," American Industrial Hygiene Conference (May, 1968).

471. Waroux, D. and Maizier, B., "Electrical Properties of Flames Used for Automatic Control of Burners," Gas (Rome) 16(10), 322-7 (1966).

472. Wasser, J. H., Hangebrauck, R. P. and Schwartz, A. J., "Effect of Air-Fuel Stoichiometry on Air Pollutant Emissions from an Oil-Fired Test Furnace," J. Air Pollution Control Assn., 18(5), 332-37 (May, 1968). (Duplicate 668).

473. Watson, K. S., et al., "Further Investigation of Electrostatic Precipitators for Large Pulverized Fuel-Fired Boilers," Air & Water Pollution 10(9), 573-83 (September, 1966).

474. Wollmann, Edmund F., "Purification and Filtration of Exhaust Gas," U.S. 3,392,968 (July, 1968).

475. Austin, H. C., Southern Cal. Edison Co., Private communication.

476. Chaikivsky, M. and Siegmund, C. W., "Low-Excess-Air Combustion of Heavy Fuel-High Temperature Deposits and Corrosion," Paper No. 64 WA/CD-2.

477. Cooper, P. W. and Marek, C. J., "Design of Blue Flame Oil Runners Utilizing Vortex Flow or Attached Jet Entrainment," API Report No. 1723,A.

478. Gosselin, A. E., Jr., "Pilot Plant Investigation of the Bay Filter House for Control of Visible Stack Emissions from Oil Fired Steam Electric Generating Stations," Proceedings from Am. Power Conf. 1964.

479. Institute of Gas Technology - IGT Services to Industry.

480. Monroe, E. S., Jr., "Improving Combustion with Heavy Fuel Oils," Oil & Gas Journal 64, No. 48, 66-69 (Nov. 1966).

481. Nicholls, J. E., et al., SAE International Automotive Engineering Congress, Detroit, Jan. 13-17, 1969, Paper No. 690018.

BIBLIOGRAPHY (PRELIMINARY 1/69)

482. Novobilski, J. A., "Top Steam Plant Performance Depends on a Good Test and Results Program," Combustion, Feb. 1967.

483. Connolly, T. J., "Formation of Oxides of Nitrogen in Gas Fuel Heaters," NAPCA Document No. 5970.

Kinetics and Modelling

500. Allen, E. R., "Reaction of Methyl and Acetyl Radicals with the Oxides of Nitrogen," Ber. Bunsenges. Phys. Chem. 72(2), 227-33 (May, 1968).

501. Applebaum, D., Harteck, P. and Reeves, R. R., "The Chemiluminescent NO--O-Atom Reaction," Photochem. Photobiol. 4(6), 1003-6 (1967).

502. Ammann, L. I., et al., Paper WWS/CI 65(4), Western States Sect. Combustion Inst. (1965).

503. Antonishin, N. V., Borodulya, V. A., Gulyuk, A. M., Zabrodskii, S. S. and Nemkovich, V. A., "Combustion of Liquid and Gaseous Fuels in a Fluidized Bed of Fine-Grained Particles and Utilization of the Gas Heat," Fiz. Goreniya, Akad. Nauk Ukr. SSSR, Respub. Mezhvedom, 20-5 (1966).

504. Ashmore, P. G. and Burnett, M. G., "Concurrent Molecular and Free-Radical Mechanisms in the Thermal Decomposition of Nitrogen Dioxide," Trans. Faraday Soc. 58, 253-61 (1962).

505. Ashmore, P. G., "The Reaction of NO & O_2," Trans. Faraday Soc. 58, 685 (1962).

506. Ashmore, P. G. and Levitt, B. P., "Thermal Decomposition of Nitrogen Dioxide," Research Correspondence 9(6), S25-S26 (1956).

507. Basevich, V. Ya. and Kogarko, S. M., "Kinetic Calculations of Low-Temperature Flames of Oxygen with Hydrogen and Carbon Monoxide," Fiz. Goreniya Vzryva 3(1), 98-104 (1967).

508. Beauseigneur, G., "Fuels and Products of Combustion. Temperature of Combustion," Rev. Gen. Therm. 6(71), 1435-44 (1967).

509. Beattie, I. R., et al., "Dinitrogen Trioxide. Part I. Stability in the Gaseous Phase," Chem. Soc. J., 1681-1686 (1957).

510. Beer, J. M., "Significance of Modelling," Inst. Fuel J., 39(310), 466-73 (November, 1966).

511. Bhaduri, D., "Theoretical Study of Coal Dust Flame," Indian J. Technology, 4(11), 322-6 (November, 1966).

BIBLIOGRAPHY (PRELIMINARY 1/69)

512. Bienstock, D., Amsler, R. L. and Bauer, E. R., Jr., "Formation of Oxides of Nitrogen in Pulverized-Coal Combustion," Amer. Chem. Soc., Div. Fuel Chem., Preprints 10(1), 1-30 (1966).

513. Bodenstein, M., "Bildung und Zersetzung der Höheren Stickoxyde," Z. Physik Chem. 100, 68-121 (1922).

514. Bonnell, J. M., "Conditions for Oscillatory Combustion in Annular Gas Combustor," Combustion Inst. Paper WSS/CI-67-36, 17 (October 30-31, 1967).

515. Boubel, R. W. and Ripperton, L. A., "Oxides of Nitrogen and Unburned Hydrocarbons Produced During Controlled Combustion," Air Pollution Control Assn., 15(6), 270-3 (June, 1965).

516. Brinkley, S. R., et al., "Thermodynamics of the Combustion Products of Kerosene with Air," Bureau of Mines Report, Px. 107/3 (1953).

517. Brocklehurst, B. and Jennings, K. R., "Reactions of Nitrogen Atoms in the Gas Phase," Progr. React. Kinet. 4, 1-36 (1967).

518. Brunnemann, H., "Effect of the Presence of Nitrogen on the Combustion Temperature of Gas Mixtures," Brennst.-Waerme-Kraft 19(7), 344-9 (1967).

519. Bufalini, J. J. and Stephens, E. R., "Thermal Oxidation of Nitric Oxide in Presence of Ultraviolet Light," Air and Water Pollution, 9(3), 123-8 (March, 1965).

520. Camac, M. and Feinberg, R. M., "Formation of NO in Shock-Heated Air," 11th Symp. Combustion, 137-44 (1966).

521. Carabogdan, I., "Beziehungen Zwischen der Verbrennungsgeschwindigkeit von Partikeln fester Brennstoffe und dem Sauerstoffgehalt des Umgebenden Raumes," Rev. Roumaine des Sciences Techniques-Serie Electrotechnique et Energetique, 12(2), 279-89 (1967).

522. Caretto, L. S., Sawyer, R. F. and Starkman, E. S., "The Formation of NO in Combustion Processes," Report No. TS-68-1, Prepared for Presentation at 1968 Tech. Meeting, Central States Section of Combustion Institute; (Duplicate 632).

523. Cescotti, R., "Burners and Flame Technology," Inst. Fuel-J 41(325), 77-84 (February, 1968).

524. Chandler, J. M., "Effects of Engine-Operating Variables on the Composition of Automotive Exhaust Gases," Proc. Am. Petroleum Inst., Section III, 38, 324-35 (1958).

525. Clough, P. N., et al., "Formation of Vibrationally Excited N_2O in the Reaction of N Atoms with NO_2," Discussions of the Faraday Society, 44, 205-207 (1967).

BIBLIOGRAPHY (PRELIMINARY 1/69)

526. Corcoran, W. H., "Mechanism in the Oxidation of Parts-Per-Million Quantities of Nitric Oxides," Ind. Eng. Chem., Fundam. 7(1), 184 (1968).

527. Cullis, C. F., Henson, R. M. and Trimm, D. L., "The Kinetics of the Homogeneous Gaseous Oxidation of Sulfur Dioxide," Proc. Roy. Soc., Ser. A, 295(1440), 72-83 (1966).

528. Cullis, C. F., Henson, R. M. and Trimm, D. L., "Reactivity of Sulphur Dioxide Towards Oxygenated Free Radicals," Combustion & Flame, 11(2), 150-4 (April, 1967).

529. Dauba, J. L., "Maximum Temperatures Attainable in Combustion of Carbon and Methane in Air," Genie Chim. 92(4), 102-10 (1964).

530. De Smete, M. G., "Fundamental Processes of Combustion," Rev. Assn. Fr. Tech. Petrole, 184, 19-36, 36-7 (1967).

531. Dioszeghy, D., "Theoretical and Practical Development of Gas-Flame Research," Freiberg. Forschungsh., B No. 120, 183-200 (1967).

532. Discussions of the Faraday Society -
    "Radiation Chemistry", 12 (1952).
    "The Study of Fast Reactions," 17 (1954).
    "Chemical Reactions in the Atmosphere", 37 (1964).

533. Dmitriev, M. T., "Application of Radiation Chemistry to the Study of the Nitrogen-Oxygen System", Zh. Prikl. Khim., 41(5), 973-82 (1968).

534. Drago, R. S., "Reactions of Nitrogen (11) Oxide," Advances in Chemistry Series #36, 143-149 (1962).

535. Essenhigh, R. H., "Combustion Phenomena in Industrial Flames: The Rosin Equation," Ind. Eng. Chem., 59(7), 52-9 (1967).

536. Eyzat, P., "Etude Experimental et Theorique de la Formation des Oxydes d'Azote Dans Les Motuers," Revue de L'Institut Francais de Petrole, 22(4), 689-712 (April, 1967).

537. Eyzat, P., et al., "A New Look at NO_x Formation in Internal Combustion Engines," SAE Report #680124. (Duplicate 420).

538. Eyzat, P. and Guibet, J. C., "Simulating the Formation of Nitric Oxide During Combustion in an Engine," Rev. Inst. Fr. Petrole Ann. Combust. Liquides, 22(10), 1530-48 (1967).

539. Fendell, F. E., "Asymptotic Treatment of Premixed Flame Structure with Diffusion", Amer. Inst. Aeronaut. Astronaut, 5(4), 808-9 (1967).

BIBLIOGRAPHY (PRELIMINARY 1/69)

540. Fendell, F. E., "Flame Structure in Initially Unmixed Reactants under One-Step Kinetics," Chem. Eng. Sci., 22(12), 1829-37 (1967).

541. Fenimore, C. P., "Chemistry in Premixed Flames," The International Encyclopedia of Phy. Chem. and Chemical Physics (1964).

542. Fenimore, C. P. and Jones, G. W., "Nitric Oxide Decomposition at 2200-2400°K," J. Phys. Chem. 61, 654-7 (1957).

543. Field, M. A., et al., "Combustion of Pulverized Coal," The British Coal Utilization Research Association (1967).

544. Fristrom, R. M. and Westenberg, A. A., "Flame Structure," (Book), McGraw Hill (1965). (Duplicate 548).

545. Frank-Kamenitskii, D.A., "Diffusion and Heat Exchange in Chemical Kinetics," Princeton University Press (1955).

546. Freedman, E., et al., "Decomposition Rate of Nitric Oxide Between 3000 and 4300°K," Journal of Chemical Physics, 34(4), (April, 1961).

547. Frisch, M. A. and Margrave, J. L., "The Heat of Formation of Nitric Oxide," J. Phys. Chem., 69(11), 3863-6 (1965).

548. Fristrom, R. M. and Westenberg, A. A., "Flame Structure", McGraw Hill (1965). (See Reference 544).

549. Fukui, Syozo, "Hygienic Chemical Studies of Noxious Gases. XI. The Mechanism of Reaction Between Nitrogen Oxides and Ammonia," Public Health Lab., 13(1), 22-8 (1967).

550. Gaydon, A. G., et al., "Flames, Their Structure, Radiation and Temperature," 13, 302, Chapman and Hill, Ltd. (1960).

551. Gaydon, A. G., "The Use of Shock Tubes for Studying Fundamental Combustion Processes," Symp. Combust. 11, 1-10 (1966).

552. Giese, C. F., "The Reaction $O^+ + N_2 \longrightarrow NO^+ + N$ In Iron Molecule Reaction in the Gase Phase," Advances in Chemistry, Series #58, 20-27 (1966).

553. Gilbert, N., et al., "Fixation of Atmospheric Nitrogen in a Gas Heated Furnace," I&E Chem., 40(9), 1719-1723 (September, 1948).

554. Glick, H. S., et al., "Single-Pulse Shock Tube Studies of the Kinetics of the Reaction $N_2 + O_2 \rightleftharpoons 2\ NO$ Between 2000-3000°K," J. Chem. Physics, 27(4), 850-857 (October, 1957).

BIBLIOGRAPHY (PRELIMINARY 1/69)

555. Gray, W. A. and Chamberlain, C. T., "Combustion of Coal in Oxygen," Nature 216(5121), 1245 (1967).

556. Greig, J. D. and Hall, P. G., "Thermal Oxidation of Nitric Oxide at Low Concentrations," Proc. Faraday, Inc., 655-661 (1967 or 1968).

557. Grumer, J., et al., "Effect of Recycling Combustion Products on Production of Oxides of Nitrogen, Carbon Monoxide and Hydrocarbons by Gas Burner Flames." 16th Annual Meeting of A.I.Ch.E. New York, Preprint #37A (November 26-30, 1967).

558. Haagen-Smit, et al., "Spectroscopic Analysis of Industrial Emissions for NO, NO_2 and SO_2," Inst. J. Air Pollution, 2, 159-166 (1959).

559. Haese, U., "Present-Day Measuring Technique and Recent Results of International Flame Research," Zem.-Kalk-Gips, 56(6), 257-66 (1967).

560. Hamming, W. J., "Control of Photochemical Smog by Alteration of Initial Reactant Ratios," J APCA, 16(6), 317-323 (1966).

561. Hanby, V. I., "Effect of Gaseous Oscillations on the Combustion Rate of Solid Fuel Particles," Fuel Soc. J., Univ. Sheffield, 18, 44-9 (1967).

562. Hangebrauck, R. P., et al., "Emissions of Polynuclear Hydrocarbons and other Pollutants from Heat Generation and Incineration Processes," Journal of APCA, 14(7) (July, 1964).

563. Harding, J. W., "Kinetics of Catalytic Decomposition of Nitric Oxide," Order No. 61-4303, 84; Discussion Abstr. 22, 1538 (1961).

564. Harker, J. H., "Calculation of Equilibrium Flame Gas Compositions," Inst. Fuel, 40(316), 206-13 (May, 1967).

565. Hasche, R. L., et al., "Studies on the Ratio of Oxidation of NO. II. The Velocity of the Reaction Between NO + OCO° + 30°," J. Am. Chem. Soc., 47, 1207 (1925).

566. Hedley, A. B., "Factors Affecting the Formation of Sulfur Trioxide in Flame Gases," J. Inst. Fuel, 40(315), 142-51 (1967).

567. Heicklen, J. and Cohen, N., "Role of Nitric Oxide in Photochemistry," Advan. Photochem., 5, 157-328 (1968).

568. Herron, J. T. and Huie, R. E., "Reaction of Atomic Nitrogen with Carbon Dioxide," J. Phys. Chem., 72(6), 2235-6 (1968).

569. Hicks, D., "Oxides of Nitrogen," Brit. Coal Util. Res. Assoc. Gaz., 62, 7-11 (1967).

BIBLIOGRAPHY (PRELIMINARY 1/69)

570. Himmelblau, D. M., Jones, C. R. and Bischoff, K. B., "Determination of Rate Constants for Complex Kinetics Models," Ind. Eng. Chem., Fundam. 6(4), 539-43 (1967).

571. Hoare, D. E., "Reactions of Methyl Radicals with NO," Canadian J. of Chem., 40, 2012-2016 (1962).

572. Hottel, H. C., "Burning in Laminar and Turbulent Fuel Flames," 4th Symp.on Comb., 97-112 (1953).

573. Hottel, H. C., et al., "Diffusion in Laminar Flame Jets," 3rd Sym. on Comb., Flame and Explosion Phenomena 254-266 (1949).

574. Howard, J. B. and Essenhigh, R. H., "Mechanism of Solid-Particle Combustion with Simultaneous Gas-Phase Volatiles Combustion," Symp. Combust., 11, 399-408 (1966).

575. Illingworth, W. R. and Jackson, E. W., "Calculation of Instantaneous Combustion Rates from Experimental Data Obtained from Controlled Mixing History Furnace," Fuel Soc., 18, 56-60 (1967).

576. Ivanov, V. N., "Study of Decomposition Kinetics of Nitric Oxide by the Method of Absorption Spectroscopy," Pet. Inst., Krasnodar, 27(1), 35-7 (1963).

577. *Jaffe, L. S., "The Biological Effects of Ozone on Man and Animals," Am. Industr. Hyg. Assoc. J. 28(267) (May-June, 1967).

578. *Jaffe, L. S., "The Biological Effects of Photochemical Air Pollution on Man and Animals," Am. J. Public Health, 57(8), 1269 (August, 1967).

579. *Jaffe, L. S., "The Effects of Photochemical Air Pollutants on Vegetation with Relation to the Air Quality Requirements," J. Air Pollut. Contr. Assoc., 17(1), 38 (January, 1967).

580. *Jaffe, L. S., "The Effects of Photochemical Oxidants on Materials," J. Air Pollut. Assoc., 17(6), 375 (June, 1967).

581. *Jaffe, L. S., "Photochemical Air Pollution: Its Effects on Men and Animals. I. General Characteristics and Community Concentrations," Arch. Env. Health, 15(782) (December, 1967).

582. *Jaffe, L. S., "Photochemical Air Pollution: Its Effects on Men and Animals. II. Adverse Effects," Arch. Env. Health, 16(241) (February, 1968).

---

* References 577-582 (Jaffe) are general background

BIBLIOGRAPHY (PRELIMINARY 1/69)

583. Karp, I. N., Soroka, B. S., Dashevskii, L. N. and Pis'mennaya, S. D., "Calculation of Thermodynamic Equilibrium for Combustion Products of Methane-Oxidizing Mixtures by Electronic Computers," Teplofiz. Vys. Temp. 5(1), 69-78 (1967).

584. Kaufman, F., et al., "Kinetics of Decomposition of Nitric Oxide", J. Chem. Phys., 21, 151 (1953).

585. Kaufman, F., et al., "Thermal Decomposition of NO", J. Chem. Physics, 23(9), 1702-7 (September, 1955).

586. Grover, S. S. (M. W. Kellogg Co.), "Application of Computers in Chemical Reaction Systems," Catal. Rev. 1(1), 153-64 (1967).

587. Khan, A. U., Pitts, J. N., Jr. and Smith, E. B., "Singlet Oxygen in the Environmental Sciences. The Role of Singlet Molecular Oxygen in the Production of Photochemical Air Pollution," Environ. Sci. Technol., 1(18), 656-7 (1967).

588. Kobayashi, Y., Abe, T., Takeno, H., Kanno, S., Fukui, S. and Naito, S., "Contribution of Engine Exhausts to Urban Atmospheric Pollution at a Street of Heavy Traffic Density in Yokohama," Bunseki Kagohu, 12(11), 1057-62 (1963).

589. See reference 626.

590. Lavrov, N. V., "Physicochemical Mechanism of Natural Gas Combustion," Teor. Prakt. Szhiganiya Gaza, Nauch-Tekh. Obshchest. Energ. Prom. 3, 136-50 (1967).

591. Le Bouc, F., "Etude Aerothermochimique des Fours et Chaudieres", Inst. Francais de Petrole et Annales des Combustibles Liquides, 22(5), 849-92 (May, 1967).

592. Lewis and von Elbe, "Combustion Flames and Explosions of Gases," Academic Press (1961).

593. Liao, Shih-Chien and Chin, Hui-Chu., "Catalytic Phenomena in Combustion Process. I. Role of Water in Combustion Process," Chung-Kuo K'o Hsueh Yuan, Ying Yung Hua Hsueh Yen Chin Chi K'an, 16, 44-50 (1966).

594. Lin, I. K. H., "Applied Kinetics," Ind. Eng. Chem., 60(5), 61-82 (1968).

595. Morgan, A. C., "The Combustion of Methane in a Jet-Mixed Reactor," D/ Sc. Thesis, M.I.T. (1967).

BIBLIOGRAPHY (PRELIMINARY 1/69)

596. Lozano, E. R., Walter, W., Jr. and Hochheiser, S., "Air Pollution Emissions from Jet Engines," J. Air Pollut. Contr. Ass. 18(6), 392-4 (1968).

597. Mc Evan, M. J., "Radical Concentrations and Decays in Lean Hydrogen-Nitrogen-Oxygen Flames," Combustion Flame, 11, 63 (1967).

598. Mayer, E., et al., "Survey of the Role of Chemistry in Premixed Combustion Phenomena," U.S. Scientific Research, Office of, PB-151,238 (1957).

599. Mayer, S. W., "Computed Activation Energies for Reactions of O_2, N_2, NO, N_2O, CO + CO_2," Aerospace Corp., El Segundo, California, Lab Operations, Contract F04695-67-C-0158, TR-0158, CFSTI, DDC: AD665473.

600. Merryman, E. L. and Levy, A., "Kinetics of Sulfur-Oxide Formation in Flames," Air Pollution Control Assn., 17(12), 800-6 (December, 1967).

601. Mirzoeva, L. M., "Thermodynamic Equilibrium Composition and Thermodynamic Parameters of Reaction Products from Nitrogen-Oxygen Mixtures at High Temperatures," Izv. Akad, Nauk Azerb. SSR, Ser. Fiz-Tekh. Mat. Nauk, 6, 70-5 (1967).

602. Mullaney, G. L., "Formation of NO_x in Complex Flames Using a Shock Turbo Technique or NO_x Formation in Autoignition of Liquid Fuel Sprays," Ind. Eng. Chem., 52, 529-32 (June, 1960).

603. Nakashiro, F., "Combustion Rate of Low-Grade Coal with Air in a Fluidized-Bed Reactor," Kagaku Kogaku 27(12), 957-62 (1963).

604. Nebel, G. J. and Jackson, M. W., "Some Factors Affecting the Concentration of Oxides of Nitrogen in Exhaust Gases from Spark Ignition Engines," J. Air Pollution Control Assoc., 8, 213-19 (1958).

605. Nesterenko, V. B. and Tverkovkin, B. E., "Kinetics of Chemical Reactions of the System $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ in Flow," Vestsi Akad. Navuk Belarusk. SSR, Ser. Fiz-Tekhn Navuk, 2, 12-19 (1966).

606. Nesterenko, V. B. and Tverkovkin, B. E., "Kinetic Equations of Chemical Reactions in Flow of the $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ System," Vestsi Akad. Navuk Belarusk, SSR, Ser. Fiz-Tekhn Navuk, 1, 34-43 (1966).

607. Newhall, H. K., "Kinetics of Engine Generated NO_x and CO," Mtg. of the Central States Section of the Combustion Institute (March, 1968).

BIBLIOGRAPHY (PRELIMINARY 1/69)

608. Newhall, H. K., "Theoretical and Experimental Investigation of Chemical Kinetics During Rapid Expansions of High-Temperature Combustion Products," Diss. Abstr. B 28(4), 1466-7 (1967).

609. Noyes, W. A., Hammond, G. S. and Pitts, J. N., Advances In Photochemistry Vols. 1, 2, 3 and 4.

610. Markstein, G. N., "Non-Study Flame Propagation," Pergamon Press, Macmillian Co. (1964).

611. Palmer, H. B., "The Rosin Equation and Combustion Intensity in Gaseous Flames," Ind. Eng. Chem. 60(3), 79 (1968).

612. Pannetier, G., Rev. Inst. Franc. Petrol. 4, 166-79, 207-239 (1949).

613. Pearson, J. and Fellinger, R., "Thermodynamic Properties of Combustion Gases," Iowa State University Press, Ames, Iowa, 1965, 230p. $7.50.

614. Peskin, R. L. and Yeh, P. S., "Results from a Theory of Fuel Drop Ignition," Intern. Aerospace Abstr. 6(6), 970-1 (1966).

615. Pitts, J. N. et al., "Singlet Oxygen in the Environmental Sciences. II. Singlet Molecular Oxygen and Photochemical A.P.," Preprint as submitted to Esso Sci. Tech. 7/17/67.

616. Polak, L. N., "Report Yields of NO Up to 8% From Reaction of $N_2 + O_2$ in a DC Plasma Jet," Akad. Nauk, S.S.S.R., Inst. Nef. Sinteza, 132-150 (1965).

617. Portio, G., Progress in Reaction Kinetics, 1967, Pergamon Press, 1st ed.

618. Reisig, V. A. et al., "The High Temperature Fixation of NO_x," Khim. Vys. Energ. 1(6), 589-91 (1967).

619. Richter, G. N. et al., "Oxides of Nitrogen in Combustion-Investigations in a Premixed Flame," Chem. Eng. Science 17, 813-823 (1962).

620. Richter, G. N. et al., "Oxides of Nitrogen in Combustion--Effects of Pressure Perturbations," Journal of Chemical & Engineering Data 8, No. 2, 215 (Apr. 1963).

621. Richter, G. N. et al., "Oxides of Nitrogen in Combustion,Premixed Flame," Combustion & Flame 6, No. 1, 1-8 (Mar. 1962).

BIBLIOGRAPHY (PRELIMINARY 1/69)

622. Richter, G. N., Wiese, N. C. and Sage, B. H., "Oxides of Nitrogen in Combustion Turbulent Diffusion Flame," J. Chem. & Eng. Data 6, 377-84 (July 1961).

623. Ripley, D. L. and Gardiner, W. C., Jr., "Chemical Kinetics of Shock-Initiated Combustion of Hydrogen at Low Temperatures and High Pressures," Combustion Inst. (Western States Sec)--Paper WSS/CI 67-28 for Fall Meeting Oct. 30-31, 1967, 29p.

624. Rogers, E. and Sage, B. H., "Some Studies of the Oxides of Nitrogen," Monthly Research Rept. of the Office of Naval Research, Jan. 1952.

625. Rosenberg, R. B., et al., "The Different Effects of Flame Chemistry on the Formation of Ethylene and the Oxides of Nitrogen in Flames," (informal copy).

626. Rosenberg, R. B. and Hacker, D. S., "Formation of Nitrogen Oxides in Aerated Methane Flames," Amer. Chem. Soc., Div. Fuel Chem. Preprints 10(3), 91-103 (1966).

627. Rosin, P. O., "Concerning the Rosin Combustion Intensity Equation," Braunkohle 24, 241 (1925); Proc. Conf. (Intl.) Bituminous Coal 1, 838 (1925).

628. Rozlovskii, A. I. and Rodin, E. P., "High-Temperature Quenching of Nitric Oxide," Dokl. Akad. Nauk SSSR 177(2), 397-400 (1967).

629. Rozlovskii, A. I., "The Kinetics and Mechanism for the Decomposition of Nitric Oxide," Zhur. Fiz. Khim. 30, 1349-55 (1956).

630. Sage, B. H., "Formation of Oxides of Nitrogen During Combustion at Atmospheric Pressure," (15th Progress Rept.: Jan. 1 to June 30, 1967), Preprint, Calif. Inst. of Tech., Pasadena, Chem. Eng. Lab., 24p., 1967.

631. Sanderson, R. T., "Multiple and Single Bond Energies in Inorganic Molecules," J. Inorg. Nucl. Chem. 30(2), 375-93 (1968).

632. Sawyer, R. F., et al., "The Formation of Nitric Oxide in Combustion Processes," Meeting of the Central States Section of the Combustion Institute, March 1968. (Duplicate 522).

633. Sawyer, R. F., "Fundamentals of Combustion," Univ. Calif. College of Eng., Berkeley, Calif., June 1967, 38p.

BIBLIOGRAPHY (PRELIMINARY 1/69)

634. Sawyer, R. F. and Starkman, E. S., "Gas Turbine Exhaust Emissions," SAE #680462 (May 20-24, 1968).

635. Schonfeld, E., "Computer Calculated Concentrations in the Reaction of Nitrogen and Oxygen," J. Chem. Educ. 45(3), 173-5 (1968).

636. Seagrave, R. C., et al., "Oxides of Nitrogen in Combustion--Some Microscopic Measurements," Combustion & Flame (8), 11 (1964).

637. Seagrave, R. C. and Sage, B. H., "Oxides of Nitrogen in Combustion: Oscillatory Combustion at Elevated Pressure," Combustion & Flame 9, No. 1, 7-18 (Mar. 1965).

638. Seagrave, R. C. and Sage, B. H., "Some Phase Relationship in Oscillatory Combustion," Combustion & Flame 10, 101-111 (June 1966).

639. Seemann, V., "Some Aspects of Combustion Kinetics; Analytical Survey," U.S. Govt. Res. Develop. Rept. 41(4), 128 (1966).

640. Seery, D. J. and Bowman, C. T., "Shock Tube Study of Methane Oxidation," Am. Chem. Soc.--Div. Fuel Chem. 11, No. 4, papers for meeting Sept. 10-15, 1967, 82-95.

641. Sensenbaugh, J. D., and Jonakin, J., "Effect of Combustion Conditions on Nitrogen Oxide Formation in Boiler Furnaces," ASME Paper 60-WA-334, 1960.

642. Serdyuk, L. S. and Tabachnikov, A. G., "Thermodynamic Properties of Nitrogen Oxide at 200-2000°K and Up to 1000 Bars," Inzh.-Fiz. Zh. 13(1), 114-17 (1967).

643. Shelef, M. and Otto, K., "Appearance of Nitrous Oxide in the Catalytic Reduction of Nitric Oxide by Carbon Monoxide," J. Catal. 10(4), 408-12 (1968).

644. Singer, J. M., et al., "Flame Characteristics Causing Air Pollution: Production of Oxides of N + CO," RI (Rept. of Investigations) #6458, Bureau of Mines, U.S. Dept. of the Interior, 1967.

645. Slutsky, S., Tamagno, J. and Fruchtman, I., "Analysis of Hydrocarbon Air Combustion Flames," Intern. Aerospace Abstr. 6(18), 3264 (1966).

646. Smith, D. S., Sawyer, R. F. and Starkman, E. S., "Oxides of Nitrogen From Gas Turbines," J. Air Poll. Control Assoc. 18(1), 30-5 (Jan. 1968).

BIBLIOGRAPHY (PRELIMINARY 1/69)

647. Soete, G. De, "Fundamental Processes of Combustion," Rev. Assoc. Fr. Tech. Petrole, No. 184, 19-36, discussion 36-7 (1967).

648. Sole, M., "The Kinetics and Mechanism of Nitric Oxide Oxidation," Collection Czech. Chem. Commun. 29(9), 2227-30 (1964).

649. Sorenson, S. C., et al., "Kinetics of Hydrocarbons in Engine Exhaust Systems," Meeting of the Central States Section of the Combustion Institute, March 1968.

650. Spealman, M. L., et al., "The Reactions of Some Oxides of Nitrogen with Atomic Oxygen and Nitrogen," J. Am. Chem. Soc. 57, 1474-1476 (1935).

651. Starkman, E. S., "Fundamental Processes in NO and CO Production from Combustion Engines," XII Congres International des Techniques de l'Automobile, 2-21.

652. Starkman, E. S., et al., "Thermodynamic Properties of CH_4 and Air, and Propane and Air for Engine Performance Calculated," SAE #670466, May 15-19, 1967.

653. Steacie, E. W. R., "Atomic and Free Radical Reactions," 2nd Ed., Vol. I and II, Reinhold Publishing, 1954.

654. Stezhenskii, A. I. and Luk'yanchikov, V. S., "Formation of Nitric Oxide in Combustion Chambers of Gas-Turbine Engines," Fiz. Goreniya, Akad. Nauk Ukr. SSR, Respub. Mezhvedom. Sb., 91-3 (1966).

655. Stezhenskii, A. I., Luk'yanchikov, V. S. and Protsenko, V. B., "Oxidation of Nitrogen During Combustion of Methane-Nitrogen-Oxygen Mixtures," Khim. Prom. Ukr. (1), 7-9 (1967).

656. Stopperka, K., Wolf, F. and Suess, G., "Gas-Phase Reaction of Nitrogen Dioxide and Sulfur Dioxide," Z. Anorg. Allg. Chem. 359(1-2), 14-29 (1968).

657. Thermodynamic Properties of the Elements. Advances in Chemistry Series No. 18 (1956).

658. Thermodynamics and Thermochemistry-Bulletin of. Section of Physical Chemistry, International Union of Pure and Applied Chemistry, March 1967.

659. Thring, M. W., Science of Flames and Furnaces, 2nd ed. 248-54, Wiley, N. Y., 1962.

BIBLIOGRAPHY (PRELIMINARY 1/69)

660. Tiggelen, P. van and Duval, A., "The Concept of a Mean Temperature in the Flame Reaction Zone," Bull. Cl. Sci., Acad. Roy. Belg. 53(4), 326-65 (1967).

661. Tipper, C. H. F., Oxidation and Combustion Reviews, 1, Elsevier Publishing Co., Amsterdam; New York, 1965, 344p.

662. Trotman, A. F., et al., "Tables of Bimolecular Gas Phase Reactions," Superintendent of Documents.

663. Vardi, J. and Biller, W. F., "Thermal Behavior of Exhaust Gas Catalytic Convertor," Indus. & Eng. Chem.--Process Design & Development 7, No. 1, 83-90 (Jan. 1968)

664. Vickland, C. W. and Starkman, E. S., "A Consideration of the High Temperature Thermodynamics of Internal Combustion Engines."

665. Vlastaras, A. S. and Winkler, C. A., "Reaction of Active Nitrogen with Oxygen," Can. J. Chem. 45(22), 2837-40 (1967).

666. Van Mourik, J. H. C., "The Formation of Nitrous Fumes in Gas Flames," Ann. Occup. Hyg. 10(4), 305-15 (1967).

667. Vulis, L. A., "Thermal Regimes of Combustion," McGraw-Hill, New York, 1961.

668. Wasser, J. H., et al., "Effect of Air-Fuel Stoichiometry on Air Pollutant Emissions from an Oil-Fired Test Furnace," J. of APCA 18, No. 5 (May, 1968). (See Reference 472).

669. Wasser, J. H., "Effects of Combustion Gas Residence Time on Air Pollutant Emissions from an Oil-Fired Test Furnace," Presented at the National Oil Fuel Inst. Workshop, Sept. 17-18, 1968.

670. Wecker, M. and Baurer, T., "Four-Center Air Reaction," Pyrodynamics 4(1), 57-8 (1966).

671. Wilson, W. E., "Rate Constant for the Reaction $N+O_2 \longrightarrow NO+O$," J. Chem. Phys. 46 (1967).

672. Wise, H., et al., "Kinetics of Decomposition of Nitric Oxide at Elevated Temperatures. I. Rate Measurements in a Quartz Vessel," J. Chem. Physics 20, No. 1, 22 (Jan. 1952).

673. Wise, H., et al., "Kinetics of Decomposition of NO at Elevated Temperatures. II. The Effect of Reaction Products and the Mechanism of Decomposition," J. Chem. Physics 20, No. 11, 1724-7 (Nov. 1952).

BIBLIOGRAPHY (PRELIMINARY 1/69)

674. Yuan, E. L., Slaughter, J. I., Koerner, W. E. and Daniels, F., "Kinetics of the Decomposition of Nitric Oxide in the Range 700-1800°," J. Phys. Chem. 63, 952-6 (1959).

675. Zeldovich, J., "The Oxidation of Nitrogen in Combustion and Explosions," Acta Physicochimica U.R.S.S. 21(4), 577 (1946).

General Background

676. Air Pollution Control District/County of Los Angeles, "Emissions of Oxides of Nitrogen from Stationary Sources in Los Angeles County,"
    Rept. #1 - Organization and Program 1960.
    Rept. #2 - Oxides of Nitrogen Emitted by Small Sources 1960.
    Rept. #3 - Oxides of Nitrogen Emitted by Medium and Large Sources 1961.
    Rept. #4 - (Final) A Summary of Data on Air Pollution by Oxides of Nitrogen Vented from Stationary Sources 1961.

677. Air Quality Act of 1967. I. A Background to the Act. II. Complete Text of the Act., J. APCA 17, No. 2, 62-71 (Feb. 1968).

678. Combustion Symposia (International), Vol. 1 to 12, The Combustion Institute, Pittsburg, Pa.

679. Stern, A. C., Air Pollution, 2nd ed. Vols. I, II, III. Academic Press, New York, 1967-68.

680. Tabor, E. C. and Golden, C. C., "Results of Five Years' Operation of National Gas Sampling Network," Air Pollution Control Assoc. J. 15, No. 1, 7-11 (Jan. 1965).

681. U.S. Public Health Service Publications:

- 640 (1959) Health Effects of Air Pollution.

682. - 763 (1960) Atmospheric Emissions from Petroleum Refineries.

683. - 978 (1962) AP Measurements National Air Sampling Network.

684. - 979 (1964) A Selected Bibliography of AP.

685. - 999 AP-1 (1963) AP Aspects of Iron and Steel Industry.

686. AP-2 (1962) Atmospheric Emissions from Fuel Oil Combustion.

687. AP-13 (1965) Emissions from H_2SO_4 Manufacture.

BIBLIOGRAPHY (PRELIMINARY 1/69)

688. AP-17 (1967) Atmospheric Emission from Manufacture of Portland Cement.

689. AP-21 (1965) CAMP in Cincinnati.

690. AP-23 (1966) CAMP in Washington, D.C.

691. AP-24 (1966) Emissions from Coal Combustion.

692. AP-27 (1966) Emissions from Nitric Acid Manufacture.

693. (1966) Interstate AP Study, Phase II; Air Pollutant Emission Inventory.

694. AP-29 (1966) Rapid Survey Technique for Estimating Community AP.

695. AP-35 (1967) Emissions from Coal-Fired Power Plants.

696. AP-40 (1968) Air Pollution Engineering Manual.

697. AP-42 (1968) Compilation of Air Pollutant Emission Factors.

698. - 1548 (1966) Sources of Air Pollution and Their Control.

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13. ABSTRACT

→This report discusses the progress achieved during the first part of a two-phase systems study of nitrogen oxide control methods for stationary sources. A broad literature survey dealing with NO_x emissions, potential control techniques, and pertinent technical information was completed. The literature survey was complemented by field survey contacts, which led to additional information on NO_x emissions and control technique possibilities. For combustion sources, preliminary estimates for the U.S. showed about 55% of the current NO_x emissions resulting from stationary sources. The contribution of power generation to uncontrolled stationary NO_x emissions was projected to increase from 45% in 1965 to 57% in 1980 and 64% in 2000.

Existing control technology for NO_x emissions is quite limited. A number of potential NO_x control methods have been identified. Combustion modification techniques have been found to be attractive because of their relative simplicity and low cost. These modifications of operating parameters and design features affect the factors influencing NO_x emissions from combustion equipment, such as lowering peak flame temperature and the supply of oxygen. NO_x control techniques by removal from stack gases have also been studied in detail. While the established technology is very limited, some methods have been identified which may provide simultaneous control of sulfur and nitrogen oxides if technical and economic feasibility can be demonstrated. ( )

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